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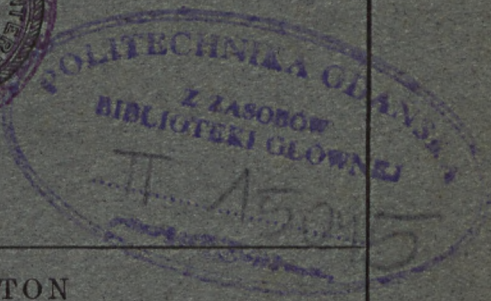
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THE ANALYSIS OF SILICATE AND CARBONATE ROCKS

A revised and enlarged edition
of Bulletin 422

BY

W. F. HILLEBRAND



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W. F. HILLEBRAND



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CONTENTS.

	Page.
Introduction.....	15
Object and scope of the present treatise.....	15
Acknowledgments.....	17
Silicate rock analysis.....	18
I. Introduction.....	18
1. Importance of complete and thorough analyses.....	18
2. The constituents occurring in silicate rocks.....	24
3. The distribution and occurrence of certain minor constituents.....	25
4. Summation of analytical results and limits of allowable error.....	30
5. Statement of analyses.....	31
6. Time needed for making an analysis.....	32
7. Useful appliances and apparatus.....	33
A. Crucible tongs.....	33
B. Radiators for volatilizing liquids and solids.....	33
C. Perforated disk for crucibles.....	35
D. Weighing scoop or trough.....	35
E. Colorimeters.....	35
a. First Survey form.....	35
b. Second Survey form (Steiger's).....	37
c. Schreiner's form.....	39
8. Preliminary qualitative analysis.....	41
9. Quality of apparatus and reagents.....	42
A. Glassware and porcelain.....	42
B. Platinum and substitutes.....	43
a. Platinum.....	43
b. Substitutes for platinum.....	44
C. Reagents.....	45
II. Methods applicable to silicate rocks.....	48
1. Introductory remarks.....	48
2. Specific gravity (porosity).....	49
General remarks.....	49
A. By suspension in water.....	50
a. Ordinary method for specific gravity.....	50
b. Method for specific gravity and porosity combined.....	51
c. Penfield's method for mineral fragments.....	53
B. Pycnometer method.....	54
a. Ordinary method.....	54
b. Refined method.....	55
C. Heavy solutions not suitable for rocks.....	57
3. Preparation of sample for analysis.....	57
A. Quantity of rock to be crushed.....	57
B. Crushing.....	57
a. Survey methods.....	57
b. Washington's method.....	59
C. Grinding.....	60
D. Abrasion of mortar and pestle.....	63
E. Weight of sample.....	64

Silicate rock analysis—Continued.

II. Methods applicable to silicate rocks—Continued.

	Page.
4. Water.—General considerations	64
A. The rôle of hydrogen in minerals	64
a. Conditions in which hydrogen may occur	65
b. Bearing of the classification on analytical procedure	67
a. Behavior of hydrogen on grinding the mineral	67
b. Behavior of hydrogen on desiccation at constant temperature	67
c. Behavior of hydrogen (expelled as water) on heating	68
c. Effect of dehydration on physical properties	69
d. Conclusion	69
B. Water taken up or lost on grinding	69
C. Importance of employing air-dry powder for analysis	71
D. Argument in favor of including hygroscopic water in the summation	72
5. Water.—Methods of determination	73
A. Indirect methods	73
a. General considerations	73
b. Methods involving the use of dehydrating agents	73
c. Methods involving the application of heat	74
a. Fractional determinations	74
b. "Loss on ignition" method for total water	76
B. Direct methods without absorption tubes—Penfield's methods	77
a. For minerals easily deprived of their water	77
b. For minerals not easily deprived of their water	78
C. Direct methods with absorption tubes	79
a. General considerations	79
b. Steiger's application of the toluene oven (for low temperatures)	81
c. Chatard's oven for temperatures up to 300° and over	82
d. Penfield's procedure (for low and high temperatures)	83
e. Dittrich and Eitel's apparatus (for low and high temperatures)	84
f. Gooch's apparatus (for high temperatures)	85
g. Kuzirian's method (for hydrous sulphates)	88
h. Merits of the several forms of apparatus	89
6. Silica—Separation from alumina, etc.	89
A. Alternative methods of decomposing the rock	89
a. General considerations	89
b. Decomposition of refractory silicates by hydrochloric acid under pressure	91
c. The boric-oxide method of Jannasch and Heidenreich	92
a. Preparation of the boric oxide	92
b. Treatment of easily decomposable silicates	92
c. Treatment of refractory silicates	92
d. Further treatment after fusion	93
e. Possible objections to the boric-oxide method	93

Silicate rock analysis—Continued.

II. Methods applicable to silicate rocks—Continued.

6. Silica—Separation from alumina, etc.—Continued.

	Page.
A. Alternative methods of decomposing the rock—Contd.	94
d. The sodium-carbonate method	94
a. Advantages of sodium carbonate over sodium-potassium carbonate	94
β. Purity of the sodium carbonate	94
γ. The fusion with normal sodium carbonate	95
δ. Fusion with sodium bicarbonate	96
ε. Treatment after fusion	97
B. Subsequent treatment	97
a. Separation of silica	97
a. Reasons for adoption of accepted procedure	97
β. Procedure in absence of notable amounts of fluorine	99
γ. Procedure with rocks and minerals containing fluorine	102
b. Ignition of silica	102
c. Correction for impurities in the silica	103
d. Accuracy of the silica determination	104
e. Composition of the residue obtained from the silica	104
f. Platinum in filtrates	105
7. Metals precipitable by hydrogen sulphide	106
8. Joint precipitation of aluminum, iron, titanium, zirconium, chromium, rare earths, phosphorus, and vanadium with and without manganese	106
A. Preliminary remarks	106
B. Precipitation without manganese	106
a. Precipitation by ammonia	106
a. Preliminary remarks	106
β. Procedure	107
b. The basic-acetate precipitation	109
a. Preliminary remarks	109
β. Procedure	110
C. Precipitation together with manganese	111
a. By ammonia and ammonium persulphate	111
a. Preliminary remarks	111
β. Procedure	112
b. By ammonia and ammonium sulphide	113
D. Recovery of unprecipitated iron and aluminum from the filtrates	113
a. After an ammonia precipitation	113
b. After a basic-acetate precipitation	113
c. After precipitation by ammonia and ammonium persulphate	114
E. Ignition of the precipitate	114
9. Determination of the oxides of iron and silicon in the precipitate obtained under 8	115
A. Preliminary remarks	115
B. Residual silica (barium)	116
a. Silica	116
b. Barium	118

Silicate rock analysis—Continued.

II. Methods applicable to silicate rocks—Continued.

9. Determination of the oxides of iron and silicon in the precipitate obtained under 8—Continued.

	Page.
C. Iron—Titrimetric determination in the ferrous state-----	119
a. Without regard to vanadium-----	119
a. Reduction of the iron by hydrogen sulphide-----	119
β. Titration of the iron and subsequent treatment of the solution-----	120
γ. Reduction with titanous sulphate-----	121
b. Having regard to vanadium-----	121
c. True value for ferric iron-----	123
D. Iron—Titrimetric determination in the ferric state-----	123
a. Preliminary remarks-----	123
b. Titration with titanous chloride-----	123
E. Iron—Gravimetric determination after separating as sulphide-----	124
a. Preliminary remarks-----	124
b. Procedure-----	124
F. Iron—Special cases-----	125
a. Glass sands-----	125
b. Ceramic clays-----	126
10. Miscellaneous separations of the oxides obtained under 8-----	126
A. Preliminary remarks-----	126
B. Recovery of aluminum, titanium, zirconium, and phos- phorus from the filtrate from iron sulphide-----	126
C. Direct fusion of the oxides obtained under 8 with sodium carbonate and borax-----	127
D. Separation of aluminum, titanium, and zirconium from iron in the ferrous state-----	128
a. By phenylhydrazine-----	128
b. By sodium acetate-----	129
a. According to Dittrich and Freund-----	129
β. According to Barbier-----	130
E. Separation of titanium and zirconium from aluminum and iron-----	130
a. According to Baskerville-----	130
b. According to Dittrich and Freund-----	131
F. Separation of aluminum from iron, etc., by a fixed caustic alkali-----	132
G. Separation of iron from aluminum, etc., as volatile chloride-----	133
H. Separation of iron from titanium by hydrogen peroxide-----	133
11. Manganese, nickel, cobalt, copper, and zinc-----	134
A. Difficulties in the way of a correct gravimetric determi- nation of manganese-----	134
B. Precipitation of the group and separation of its consti- tuents-----	135
a. The ammonium-sulphide method-----	135
a. Its advantages and disadvantages-----	135
β. Precipitation by ammonium sulphide and separa- tion of manganese and zinc from nickel, cobalt, and copper-----	135
b. Manganese and zinc-----	136
c. Nickel, cobalt, and copper-----	136

Silicate rock analysis—Continued.

II. Methods applicable to silicate rocks—Continued.

11. Manganese, nickel, cobalt, copper, and zinc—Continued. Page.

C. Colorimetric determination of manganese----- 137

a. Preliminary treatment----- 137

b. Colorimetric determination of manganese by ammonium persulphate----- 137

D. Direct titration of manganese----- 139

12. Calcium and strontium (barium)----- 140

A. Separation from magnesium----- 140

a. General considerations----- 140

b. Separation when neither calcium nor magnesium preponderates excessively----- 141

c. Ignition of the calcium oxalate----- 142

d. Separation of little calcium from much magnesium----- 142

a. Preliminary remarks----- 142

β. Modified Stolberg method----- 143

γ. Murmann's method----- 143

δ. Author's method----- 143

e. Separation of little magnesium from much calcium----- 144

B. Separation of strontium (barium) from calcium----- 144

a. By ether-alcohol----- 144

b. Other methods----- 144

C. Behavior of barium----- 145

D. Separation of barium from strontium----- 145

E. Other methods of determining calcium after precipitation as oxalate----- 146

a. Preliminary remarks----- 146

b. Volumetric method----- 147

c. By weighing as the carbonate----- 147

d. By weighing as the sulphate----- 147

e. By weighing as the fluoride----- 148

13. Magnesium----- 148

A. Precipitation----- 148

a. Conditions necessary for the production of a normal precipitate----- 148

b. Precipitation and filtration----- 149

a. First precipitation----- 149

β. Second precipitation----- 150

B. Ignition of the precipitate----- 150

C. Contamination by and removal of barium, calcium, and manganese----- 152

a. Barium----- 152

b. Calcium----- 152

a. Preferred method----- 152

β. Alternative method----- 152

c. Manganese----- 153

D. Liability to error in the average magnesium determination----- 153

14. Titanium----- 154

A. General considerations----- 154

B. Colorimetric determination with hydrogen peroxide----- 155

a. Principle of the method (Weller's) and the conditions that affect it----- 155

Silicate rock analysis—Continued.

II. Methods applicable to silicate rocks—Continued.

14. Titanium—Continued.

B. Colorimetric determination with hydrogen peroxide—Con. Page.

b. Preparation of the standard..... 157

c. The test solution..... 157

d. The color comparison..... 159

e. Correction for the color of ferric sulphate..... 160

a. By allowing for the coloring power of the iron in the test solution..... 160

β. By addition of iron to the standard..... 160

γ. By the use of phosphoric acid..... 161

f. Correction for the effect of alkali sulphates..... 161

g. Correction for the effect of vanadium..... 162

C. Gravimetric methods..... 162

a. Gooch's method..... 162

a. Description of the method..... 162

β. Gooch's method not directly applicable to rocks containing zirconium..... 163

b. Thornton's method..... 164

a. Preliminary remarks..... 164

β. Procedure..... 165

c. Baskerville's method..... 166

d. Method of Dittrich and Freund..... 166

D. Volumetric methods..... 166

a. General considerations..... 166

b. Methylene blue method..... 168

c. Ferric alum method..... 168

d. Permanganate method..... 169

15. Barium (zirconium, rare earths, total sulphur, chromium)..... 170

A. The general method..... 170

B. The method without regard to zirconium and sulphur..... 172

16. Zirconium..... 172

A. Author's method..... 173

a. Preliminary remarks..... 173

b. Procedure..... 173

B. Other methods..... 175

17. Rare-earth metals other than zirconium..... 176

A. Usual method..... 176

B. Alternative method..... 177

18. Phosphorus..... 177

A. Preliminary remarks..... 177

B. Procedure when material is ample..... 178

a. Washington's method of preliminary treatment..... 178

b. Alternative method of preliminary treatment..... 178

c. Subsequent treatment..... 178

C. Procedure when material is scanty..... 179

19. Chromium..... 180

A. Gravimetric methods..... 181

a. Author's method..... 181

b. Jakob's method..... 181

CONTENTS.

Silicate rock analysis—Continued.

II. Methods applicable to silicate rocks—Continued.

19. Chromium—Continued.

	Page.
B. Colorimetric method	182
a. Preparation and strength of standard solution	182
β. Preparation of test solution	182
γ. Comparison of colors	183
C. Comparative data	183

20. Vanadium (chromium) and molybdenum

A. Distribution of vanadium and molybdenum	184
B. Condition of vanadium in rocks	184
C. Author's method	185
a. Description of the method	185
b. Confirmatory qualitative tests	187
c. Application of the method in presence of relatively much chromium	187
D. Colorimetric method for vanadium	189

21. Ferrous iron

A. Oxidation of ferrous iron in minerals by grinding—preparation of sample	189
B. Comparison of sealed-tube and hydrofluoric acid methods—comparative worthlessness of the former in rock analysis	193
C. The modified Mitscherlich method	195
a. Strength of acid	195
β. Filling, sealing, and heating of the tube	195
γ. Reason for introducing gas and sealing as above directed	196
D. The hydrofluoric acid method	196
a. Principle of the method	196
b. Defects of the method	197
a. Oxidizability of divalent manganese by permanganate in presence of hydrofluoric acid	197
β. Extreme oxidizability of divalent iron by free oxygen in the presence of hydrofluoric acid or a fluoride	199
c. Influence of sulphides, vanadium, and carbonaceous matter on the determination of ferrous iron by the hydrofluoric-acid method	201
a. Sulphides	201
β. Vanadium	202
γ. Carbonaceous matter	203
d. The method in its various modifications	203
a. According to Pratt (modified)	203
β. According to Cooke	204
γ. According to Barnebey	205
δ. According to Treadwell	207
E. Uncertainties of the ferrous-iron determination	207

22. Alkalies

A. The J. Lawrence Smith method	207
a. Its advantages	207
b. Reagents and apparatus	208
c. Treatment of the mineral powder	208

Silicate rock analysis—Continued.

II. Methods applicable to silicate rocks—Continued.

22. Alkalies—Continued.

A. The J. Lawrence Smith method—Continued.

Page.

d. Separation of calcium and sulphuric acid..... 210

e. Precipitation of potassium..... 210

f. Sodium and lithium..... 211

a. Gooch's method for separating lithium..... 212

B. Preliminary treatment by other methods..... 213

a. The mercuric oxide method..... 213

b. The ammonium carbonate method..... 213

c. The amyl alcohol method..... 214

C. Direct separation of potassium by sodium cobaltinitrite..... 214

a. Preparation of the reagent..... 215

b. Application of the method..... 215

a. Determination as chlorplatinite..... 216

β. Determination as perchlorate..... 216

23. Carbon dioxide, carbon..... 217

A. Qualitative test for carbon dioxide..... 217

B. Quantitative test for carbon dioxide..... 217

C. Carbon..... 219

24. Chlorine..... 220

A. Condition in rocks..... 220

B. Determination of water-soluble chlorine..... 220

C. Determination of acid-soluble chlorine..... 221

a. By nitric acid..... 221

b. By nitric and hydrofluoric acids..... 221

D. Determination of chlorine by alkali fusion..... 221

25. Fluorine (silica in presence of fluorine)..... 222

A. General remarks..... 222

B. Direct quantitative determination of fluorine..... 222

a. Method of Berzelius..... 222

a. Procedure..... 222

β. Testing of the calcium fluoride..... 224

γ. Accuracy of the method..... 225

b. Determination of silica in the method of Berzelius..... 226

c. Other direct methods for fluorine..... 226

C. Indirect quantitative determination of fluorine..... 227

a. Steiger's method..... 227

b. Merwin's modification of Steiger's method..... 227

a. Introductory remarks..... 227

β. Procedure..... 228

26. Sulphur..... 230

A. Determination of the condition of sulphur in rocks..... 230

B. Quantitative method—general discussion..... 230

C. Quantitative determination in rocks..... 231

a. Total sulphur..... 231

b. Fractional determination..... 233

27. Boron..... 234

A. General remarks..... 234

B. Distillation method as modified by Chapin..... 235

a. Reagents..... 235

b. Apparatus..... 236

c. Procedure..... 236

C. Qualitative tests for boron..... 240

Silicate rock analysis—Continued.

II. Methods applicable to silicate rocks—Continued.	Page.
28. Certain constituents in minute traces.....	241
29. The gases and vapors expelled by heat.....	242
30. Special operations.....	243
A. Detection of nepheline in presence of olivine.....	243
B. Determination of "soluble" silica.....	244
Carbonate rock analysis.....	246
III. Introduction.....	246
31. Qualitative comparison of carbonate and silicate rocks.....	246
32. Mineral composition of carbonate rocks.....	248
33. Behavior toward different reagents as a means of distinguish- ing different carbonates.....	251
A. Differing solubility in tartaric and citric acids and in acid potassium sulphate.....	251
B. Distinguishing calcite from aragonite.....	251
C. Distinguishing between calcite and dolomite.....	251
IV. Refined methods of analysis.....	253
34. Silica, its separation from alumina, etc.....	253
A. Methods of decomposing the rock.....	253
a. When the inorganic residue is to be separately analyzed.....	253
b. When the inorganic residue is not to be separately analyzed.....	254
a. By solution in acid after strong ignition.....	254
β. By solution in acid after heating with sodium carbonate.....	255
B. Separation of silica.....	256
35. Aluminum, total iron, titanium (silica, manganese); precipi- tation in company with phosphorus.....	257
A. Precipitation of aluminum, iron, etc.....	257
a. Collective precipitation of aluminum, iron, manga- nese, titanium, and phosphorus by ammonium sul- phide.....	257
b. Precipitation of aluminum, iron, titanium, and phos- phorus by ammonia.....	258
c. Precipitation of aluminum, iron, titanium, and phos- phorus by the basic-acetate method.....	258
B. Treatment of the filtrates from alumina, etc.....	259
C. Solution and separation of the oxides obtained in A and B.....	259
a. Silica (barium).....	259
b. Iron.....	260
c. Titanium.....	260
d. Aluminum.....	260
36. Manganese.....	260
A. In the filtrates from 350 B.....	260
B. Separate determination of manganese.....	261
37. Copper, nickel, cobalt, lead, zinc, rare earths, chromium, vana- dium, molybdenum.....	261
38. Calcium, strontium, barium, magnesium (manganese).....	262
A. Ordinary procedures.....	262
B. Separation of little calcium from much magnesium—mag- nesite analysis.....	263

Carbonate rock analysis—Continued.

IV. Refined methods of analysis—Continued.		Page.
39. Phosphorus	-----	263
40. Ferrous iron	-----	264
A. In the absence of carbonaceous matter	-----	264
a. Ferrous iron soluble in sulphuric acid	-----	264
b. Ferrous iron in the insoluble residue	-----	265
c. Total ferrous iron	-----	265
B. In the presence of carbonaceous matter	-----	265
41. Alkalies	-----	265
42. Carbon dioxide, carbon (water)	-----	266
A. Determination of carbon dioxide	-----	266
B. Determination of carbon of carbonaceous matter	-----	266
C. Simultaneous determination of water and of total carbon	-----	267
43. Chlorine	-----	267
44. Fluorine	-----	268
45. Sulphur	-----	268
A. Tests as to its condition; determination of sulphate	-----	268
sulphur	-----	268
B. Determination of total sulphur	-----	268
a. Methods of converting sulphides to sulphates	-----	268
a. By ignition without flux	-----	268
β. By ignition with sodium carbonate	-----	269
b. Treatment after ignition	-----	269
46. Water	-----	269
A. Hygroscopic water	-----	269
B. Firmly held water	-----	270
V. Condensed analysis	-----	271
47. Decomposition and solution	-----	271
48. Silica	-----	271
49. Aluminum, iron, etc	-----	272
50. Calcium	-----	273
51. Magnesium	-----	273
52. Alkalies	-----	274
53. Carbon dioxide	-----	274
54. Sulphur	-----	274
55. Water	-----	274
56. Ignition loss	-----	274
Index	-----	275

ILLUSTRATIONS.

	Page.
FIGURE 1. Platinum-tipped crucible tongs.....	32
2. Radiator for rapid and safe evaporation.....	33
3. Device for excluding flame gases from the interior of crucibles during ignition.....	34
4. Weighing trough of platinum.....	35
5. First Survey form of apparatus for colorimetric determinations.....	36
6. Steiger's colorimeter (second Survey form).....	38
7. Schreiner's colorimeter.....	40
8. Moore's device to remove air from mineral powders.....	56
9. Ellis's mortar for crushing coarse materials.....	58
10. McKenna ore grinder.....	62
11. Penfield's tubes for water determination in minerals.....	78
12. Penfield's fire-brick and charcoal oven for use in determining water.....	79
13. Steiger's form of drying apparatus.....	81
14. Chatard's form of drying oven for water determinations.....	82
15. Tube for water determination according to Penfield.....	83
16. Modified form of Gooch tubulated platinum crucible for the determination of water.....	85
17. Arrangement, during drying, of Gooch apparatus for determining water.....	87
18. Arrangement, during fusion, of Gooch apparatus for determining water.....	88
19. Cooke's apparatus for ferrous-iron determination.....	205
20. The J. Lawrence Smith crucible for alkali determinations.....	209
21. Compact form of apparatus for determination of carbon dioxide.....	218
22. Merwin's diagram for fluorine.....	229
23. Distilling apparatus for boron.....	237

THE ANALYSIS OF SILICATE AND CARBONATE ROCKS.

By W. F. HILLEBRAND.

INTRODUCTION.

OBJECT AND SCOPE OF THE PRESENT TREATISE.

Prior to the publication of Bulletin 148 of the United States Geological Survey the literature relating to the analysis of silicates, though extensive, was so widely scattered that in no single work was there to be found, in the light of modern methods, a satisfactory exposition of the procedures to be followed or the precautions to be observed, especially in the search for some of the rarer constituents or those which, without being rare, had come to be recognized as occurring persistently in small amounts. It was not the intention to make the chapter on rock analysis in Bulletin 148 a manual on mineral or even rock analysis, but to show primarily the principles and methods by which the major part of the analyses made up to that time in the laboratory of the Geological Survey had been conducted, and thus to afford a partial measure of the trustworthiness of those analyses. At the time it was felt that the experience gained by the chemists of the Survey since the establishment of its first chemical laboratory in Denver might be useful to most chemists engaged in mineral and rock analysis. The favorable reception accorded to it by chemists led to the republication of a portion of that bulletin in more extended form as Bulletin 176, and since then other enlarged revisions have appeared under the numbers 305 and 422. Bulletins 148 and 176 treated only of the analysis of silicate rocks. In Bulletin 305 there was added a section on carbonate rocks, for the reasons that the chief carbonate rocks form a most important element in the earth's crust and that the knowledge of their composition is of moment to the geologist as well as to the cement worker, who now makes enormous use of them. The methods applied to their analysis differ in but unimportant respects from those used with the more siliceous rocks, for they are to a great extent themselves siliceous and contain essentially the same constituents, and therefore the same principles apply to both. Naturally they demand and receive briefer treatment.

The special problems often arising in the analysis of rocks of extraterrestrial origin—the more or less stony meteorites—will not be considered here. An analysis of those objects should never be intrusted to the novice but only to the chemist who has a knowledge of the comparison and properties of their peculiar mineral constituents and a judgment fit to cope with the difficult problems they present.

A suggestion was made to the author that the analysis of artificial glasses and of glazes, and possibly of other industrial silicate products, be covered in this volume. To do so, however, would involve increasing the size of the volume materially, in order to take account of the considerable number of elements occurring in such products that are not rock constituents in more than minute traces. Moreover, the elaborate treatise of J. W. Mellor¹ is available.

The third edition of Dr. H. S. Washington's "Manual of the chemical analysis of rocks," appeared just as the manuscript of this volume was completed—too late for me to benefit largely by the extended revision of the earlier texts.

I regret that no reference could be made in the text to electro-metric methods for determining iron in both the ferrous and ferric states. The subject has been well treated by J. C. Hostetter and H. S. Roberts in a recent paper.² In a companion paper H. S. Roberts³ describes the apparatus needed in applying the method. I can only urge upon all mineral analysts to consult both papers. High and low percentages of iron can be determined quickly, with high accuracy, and with fewer precautions than by the older methods, not only in sulphuric acid solution but also in hydrochloric or hydrofluoric acid as well as in mixtures of these acids.

The methods described in the later bulletins mentioned were not restricted to those actually in use at the Geological Survey, and a still further departure in this direction has been made in the present treatise. Many new methods and modifications of methods have been published in the last 10 years. Some of these may certainly be applied satisfactorily in rock analysis, and others seem promising. The most promising of the latter group have been described in the text in order to stimulate analysts to try them out, for it is well to have more than one good method for reaching a desired end. Another reason for presenting some simpler though perhaps less reliable methods is that a few of those preferred entail the use of expensive apparatus or complicated arrangements which are not at the com-

¹ A treatise on quantitative inorganic analysis, being vol. 1 of A treatise on the ceramic industries, London, Griffin & Co., 1913. Among other publications on the subject of glass analysis a paper by E. C. Sullivan and W. C. Taylor (Jour. Ind. Eng. Chemistry, vol. 6, 1914, p. 897) deserves mention.

² Jour. Am. Chem. Soc., vol. 41, 1919, p. 1337.

³ Idem, p. 1358.

mand of all analysts. However, where silicate and limestone analyses are made in number it is a saving of time and, in the end, of money to set up permanent and even expensive arrangements for convenience in determining such constituents as water, carbon dioxide, ferrous iron, and boron, and in making reductions by hydrogen.

My transfer in 1908 from the Geological Survey to the Bureau of Standards has made it impossible for me to keep closely in touch with changes that may have been made in the analytical procedures and methods of the laboratory staff of the Survey. This statement is made in order to prevent possible misconception. The present work is to be considered as a general treatise on rock analysis, based on my own views and experience, often supported by those of others, rather than as an authoritative presentation of methods now practiced or approved by the present Survey staff.

Compared with its predecessor this bulletin shows many changes and additions, with some omissions. To enumerate them all is needless. A few, however, may be mentioned.

Additions have been made to the section on chemical reagents, especially by including information on porcelain, glass, and platinum ware and substitutes for platinum ware. The greater part of the chapter on the rôle of hydrogen in minerals has been rewritten for me in the light of modern views by Dr. E. T. Wherry, of the Department of Agriculture; Dr. H. E. Merwin, of the Geophysical Laboratory of the Carnegie Institution; and Mr. Elliot Q. Adams, of the Department of Agriculture.

Sections 8 to 14, in Part II, have undergone much modification, with the introduction of descriptions of new methods for the determination of individual constituents and for the fractional separation of complex precipitates, preliminary to the determination of the components of the less complex fractions. Two new sections have been introduced here in amplification of the matter that was previously presented in section 8. A detailed procedure for determining boron is given, in order to stimulate search for this very minor and hitherto entirely neglected element.

ACKNOWLEDGMENTS.

Drs. E. T. Wherry and H. E. Merwin and Mr. Elliot Q. Adams very kindly revised the chapter on the rôle of hydrogen in minerals, and Drs. Wherry and Merwin gave friendly advice on other points. My associate, Dr. G. E. F. Lundell, of the Bureau of Standards, rendered most valuable aid by his criticisms of the preliminary text and by tests of methods. Mr. H. B. Knowles, of the Bureau of Standards, was helpful in the experimental testing of certain methods. To all these gentlemen my thanks are gratefully tendered.

SILICATE ROCK ANALYSIS.

I.—INTRODUCTION.

1. IMPORTANCE OF COMPLETE AND THOROUGH ANALYSES.

The composition of the ultimate ingredients of the earth's crust—the different mineral species which are there found and of many of which its rocks are made up—was the favorite theme of the great workers in chemistry of the earlier half of the nineteenth century, and for the painstaking care and accuracy of Berzelius, Wöhler, and others the mineralogists and geologists of to-day have reason to be thankful. Considering the limited facilities at their disposal in the way of laboratory equipment and quality of reagents, the general excellence of their work is little short of marvelous. As an outgrowth of and closely associated with the analysis of minerals came that of the more or less complex mixtures of them—the rocks—to aid whose study by the petrographer and geologist a host of chemists have for many decades annually turned out hundreds of analyses of all grades of quality and completeness. With the growth and extraordinary development of the so-called organic chemistry inorganic chemistry gradually fell into a sort of disfavor. In many, even the best, European laboratories the course in mineral analysis, while maintained as a part of the curriculum of study, became but a prelude to the ever-expanding study of the carbon compounds, which, multiplying rapidly and offering an easy and convenient field for original research and possible profit, proved more tempting to young chemists than the often worked-over and apparently exhausted inorganic field. For one student devoting his time to higher research in inorganic chemistry fifty perhaps were engaged in erecting the present enormous structure of carbon chemistry. The instruction afforded to the student in mineral analysis was confined to the ordinary separations of the commoner ingredients occurring in appreciable quantities, with little regard to supposed traces and with still less attempt to find out if the tabulated list really comprised all that the mineral or rock contained.

With the introduction of improved methods of examination by the petrographer, especially as applied to thin rock sections, and the use of heavy solutions, whereby, on the one hand, the qualitative mineral composition of a rock could be preliminarily ascertained with considerable certainty, and on the other hand chemical examination of the more or less perfectly separated ingredients was rendered possible, a great help and incentive was afforded to the few chemists engaged in rock analysis. The microscope often

obviated in part the necessity for tedious and time-wasting qualitative tests, and the heavy solutions, by permitting the concentration and separation of certain components, facilitated the detection of elements whose existence had long been overlooked.

Meanwhile, in the progress of chemistry new methods and reagents for qualitative detection and quantitative separation and estimation were gradually being devised and discovered. The belief that some well-established methods were adequate was shown to be unwarranted; some had to be discarded altogether; others were still utilizable after modification. In the light thus shed it became possible to explain many hitherto incomprehensible variations in the composition of some rock species or types, as shown in earlier analyses, and in not a few cases it appeared that the failure to report the presence of one or more elements had obscured relations and differences which more thorough examination showed to exist. (See p. 21.) Consequently there arose a feeling of distrust of much of the older work in the minds of those chemists and petrographers who were best fitted to judge of its probable qualities. This, and the incompleteness of nearly all the earlier work (and some of that of to-day, unfortunately), as shown by the largely increased list of those elements now known to enter into the normal composition of rocks, are rendering the old material less and less available to meet the increasing demands of the petrographer.¹

And yet these demands were, with few exceptions, by no means so exacting as they should have been. Frequently the analysis was intrusted to a student without other experience than that gained by the analysis of two or three artificial salts and as many comparatively simple natural minerals, and with a laboratory instructor as adviser whose experience in rock analysis might be little superior to his own. In other words, one of the most difficult tasks in practical analysis was given to a tyro, and his results were complacently accepted and were published broadcast without question. Even to those who are thoroughly familiar with the subject rock analysis is a complex and often a trying problem. Although long practice may have enabled one to do certain parts of the work almost mechanically, perplexing questions still arise which require trained judgment to meet and answer properly, and there is yet room for important work in some of the supposedly simplest quantitative determinations. If

¹ Dr. Henry S. Washington, in Professional Papers 99 (Chemical analyses of igneous rocks published from 1884 to 1913, with a critical discussion of the character and use of analyses) and 28 (The superior analyses of igneous rocks from Roth's Tabellen, 1869 to 1884, arranged according to the quantitative system of classification) of the United States Geological Survey, has done a most important work in sifting the great mass of data accumulated in the thousands of analyses published since 1869. After a systematic critical examination he has assigned to each analysis a certain value on a scale of 5. Many of these values may be incorrect, but most of them undoubtedly give a fairly true measure of the weight to be attached to the respective analyses.

the results are to have any decided value for purposes of scientific interpretation and comparison, they must be the outcome of the work of one who is able to find his way through the intricacies of an analysis in which from 15 to 25 components are to be separated and estimated with close approach to accuracy, and this a beginner can not hope to do. The conscientious chemist should have a live interest in this matter. He should work with a twofold purpose in view—that of lightening the labors of those who come after him by enabling them to use his work with less supplementary examination, and that of enhancing his own reputation by meriting encomiums on work that has stood the test of time.

How little understood may be the principles underlying the treatment of bodies so complex and the accurate separation and determination of their constituents, even when these are comparatively few, has been strikingly shown during recent years in the work of several committees of chemists charged with the investigation of the methods employed in various branches of technical chemistry involving the analysis or assay of zinc ores, slags from the smelting of copper ores, argillaceous limestones, and cements. In all cases a most woeful inability to obtain accordant results is apparent, not only among those less experienced but among those supposed to be most expert in each of the particular fields as well. Some improvement in commercial silicate analysis has resulted from the investigations set on foot and the recommendations made by these committees, and further improvement may be expected, but the situation is yet anything but satisfactory. A more marked improvement has been shown in the quality of analyses made for scientific study, but the art of analysis stands in great need of more thorough treatment in our educational institutions.

The petrographer, again, should seek to have his analyses made as complete as possible, and not, as was often the case, be content with determinations of silica, alumina, the oxides of iron, lime, magnesia, the alkalis, and water. The latter course, it is true, is entirely justifiable at times and may serve the immediate purposes of the analyses, but their incompleteness may, on the other hand, not only conceal points fruitful of suggestion to the attentive mind, but, what is of still greater importance, they may be actually misleading. Enough instances of totally inaccurate conclusions to be drawn from them have fallen under my own observation to fully justify this plea in favor of greater completeness in rock and mineral analysis made for purely scientific purposes.¹

The importance of the points indicated in the foregoing paragraph is shown by the difference between the analyses given below. The

¹ For further presentation of this subject from the viewpoint of an experienced petrographer, see Washington, H. S., *Manual of the chemical analysis of rocks*, 1919, pp. 7-17.

specimens were taken and analyzed at widely separated times and by different persons, it is true, but they were unquestionably from the same rock mass, in which, however much the relative proportions of the different mineral constituents might vary within certain limits, there can be no reason to doubt the general distribution of all the elements shown by the second analysis.

Analyses of specimens taken from the same rock mass at different dates.

	Earlier analysis.	Later analysis. ^a		Earlier analysis.	Later analysis. ^a
SiO ₂	54.42	53.70	Li ₂ O.....	Trace.	Trace.
TiO ₂		1.92	H ₂ O below 110°.....		0.80
Al ₂ O ₃	13.37	11.16	H ₂ O above 110°.....	c 2.76	2.61
Cr ₂ O ₃04	CO ₂	1.82	1.75
Fe ₂ O ₃	b 6.61	3.10	P ₂ O ₅06
FeO.....	b 3.52	1.21	SO ₃44
MnO.....		.04	F.....		.03
CaO.....	4.38	3.46	Cl.....		
SrO.....		.19		99.58	100.40
BaO.....		.62			.19
MgO.....	6.37	6.44	Less O for F.....		
K ₂ O.....	10.73	11.16			100.21
Na ₂ O.....	1.60	1.67			

^a A still more recent analysis of another of the series of rocks of which this is an example has shown that this "later analysis" is itself probably incomplete and incorrect in part—incomplete because of the probable presence of 0.2 per cent or more of ZrO₂, incorrect because of the error in Al₂O₃, resulting from having counted the ZrO₂ as Al₂O₃, and from the fact that titanium is not fully precipitable in presence of zirconium by Gooch's method (the one employed). This latter error involves both the TiO₂ and the Al₂O₃. (See 14. C. a. β, p. 163.)

^b From the fact that repeated determinations of the iron oxides in this and related rocks from the same region show always a great preponderance of ferric oxide, it is not improbable that the figures given for the two oxides in the first analysis were accidentally transposed.

^c In the published analysis it does not appear whether this is total water or, as seems probable, only that remaining above 100°.

Another instance of similar kind is given below. Here, again, certain differences are explainable by natural variations in the proportions of the constituent minerals, but it can hardly be doubted that TiO₂, BaO, SrO, P₂O₅, and SO₃ were present in both specimens in approximately the same amounts. In the earlier analysis determinations of some supposedly unimportant constituents were purposely omitted or made only qualitatively, with results that can not be otherwise than fatal to a full comprehension of the mineralogic nature of the rock.

Analyses of specimens taken from the same rock mass at different dates.

	Earlier analysis.	Later analysis.		Earlier analysis.	Later analysis.
SiO ₂	44.31	44.65	Na ₂ O.....	4.45	5.67
TiO ₂	Not est.	.95	Li ₂ O.....		Trace.
Al ₂ O ₃	17.20	13.87	H ₂ O below 110°.....	.77	.95
Fe ₂ O ₃	4.64	6.06	H ₂ O above 110°.....		2.10
FeO.....	3.73	2.94	H ₂ O by ignition.....	3.30	
MnO.....	10	.17	CO ₂11
CaO.....	10.40	9.57	P ₂ O ₅		1.50
SrO.....		a. 37	Cl.....		Trace.
BaO.....		.76	SO ₃61
MgO.....	6.57	5.15		99.11	99.92
K ₂ O.....	3.64	4.49			

^a Not entirely free from CaO.

F. W. Clarke has shown that the combined percentages of titanic and phosphoric oxides in rocks of the earth's crust, averaged from hundreds of analyses, amount to 0.8 per cent. When the determination of these is neglected the error falls on the alumina. If the alumina is then used as a basis for calculating the feldspars, it is easy to see that a very large average error in the latter may result, amounting to several per cent of the rock.

In order to emphasize more strongly the importance of completeness in analysis, a few facts brought out by the hundreds of rock analyses made in this laboratory may be cited. It has been demonstrated most conclusively that barium and strontium are almost never-failing constituents of the igneous rocks of the United States and of many of their derivatives. The amounts are usually below 0.1 per cent for each of the oxides of those metals, but higher amounts are by no means uncommon. Furthermore, the weight of barium is almost without exception in excess of that of strontium; but a still more important point is that the igneous rocks of the Rocky Mountain region, so far as examined, show much higher average percentages of both metals than the rocks from the eastern and the more western portions of the United States. The following examples serve to illustrate certain types of Rocky Mountain igneous rocks: Of seven rocks forming a Colorado series, six held from 0.13 to 0.18 per cent of BaO, while in the seventh the percentage was 0.43. The SrO ranged from 0.07 to 0.13 per cent for six and was 0.28 for that one highest in BaO. Of thirteen geologically related rocks from Montana, embracing basic as well as acidic and intermediate types, the range of BaO was from 0.19 to 0.37 per cent, with an average of 0.30 per cent. Three others of the same series contained 0.10 per cent or less, while the seventeenth carried 0.76 per cent BaO. The SrO ranged from 0.37 per cent in the seventeenth rock to an average of 0.06 for the other sixteen. Certain peculiar rocks from Wyoming carry from 0.62 to 1.25 per cent BaO and from 0.02 to 0.33 per cent SrO. Surely this concentration of certain chemical elements in certain geographic zones has a significance which future geologists will be able to interpret, if those of to-day are not.

Again, vanadium is an element which few chemists ever thought of looking for in igneous rocks, though it has long been known to occur in magnetites and other iron ores. A. A. Hayes, in 1875, reported its occurrence in a great variety of rocks and ores. To quote from Thorpe's "Dictionary of chemistry:" "It is said to be diffused with titanium through all primitive granite rocks (Dieulafait) and has been found by Deville in bauxite, rutile, and many other minerals and by Bechi and others in the ashes of plants and in argillaceous limestones, schists, and sands." It is further reported to comprise, as the pentoxide, up to 0.1 per cent of many

French and Australian¹ clays, 0.02 to 0.03 per cent of some basalts, 0.24 per cent of a coal of unknown origin, and 0.45 per cent of a coal from Peru. Still later examinations in this laboratory of about 100 rocks, chiefly igneous, covering nearly the whole continental territory of the United States, show not only its general qualitative and quantitative distribution, but that it predominates in the less siliceous igneous rocks and is absent, or nearly so, in those high in silica. In some of the more basic rocks it occurs in sufficient amount to affect seriously the figures for the oxides of iron unless separately estimated and allowed for (see 21. D. c. β , p. 202), a matter of considerable importance, because the petrographer lays great stress on accuracy in their determinations.

The same investigation also threw some light on the distribution of molybdenum, which seems to be confined to the more siliceous rocks and to occur in quantities far below those commonly found for vanadium.

Finally, had it not been my practice during all the later years of my work to look for sulphur in rocks, even when no sulphides were visible to the eye, its almost invariable presence in the form of sulphide and consequent connection with the long mystifying lack of agreement between results for ferrous iron obtained by the Mitscherlich and the hydrofluoric-acid methods might not have been suspected. (See 21. B, p. 193.)

While strongly upholding the necessity for more thorough work, necessarily somewhat at the expense of quantity, it is far from my intention to demand that an amount of time altogether disproportionate to the immediate objects to be sought should be expended on every analysis. But I maintain that, in general, the constituents which are likely to be present in sufficient amount to admit of determination in the weight of a sample usually taken for analysis—say 1 gram for SiO_2 , Al_2O_3 , etc., to 2 grams for certain other constituents—should be sought for, qualitatively at least, in the ordinary course of quantitative work, and their presence or absence noted among the results. If present in little more than traces, that knowledge alone may suffice, for it is often more important to know whether or not an element is present than to be able to say that it is there in amount of exactly 0.02 or 0.06 per cent. In the tabulation of analyses a special note should be made in case of intentional or accidental neglect to look for substances which it is known are likely to be present. Failure to do this may subject the analyst to unfavorable criticism when, at some future time, his work is reviewed and the omissions are discovered by new analyses.

¹ J. C. H. Mingaye has confirmed its wide distribution in Australian rocks, coals, etc. (Records Geol. Survey New South Wales, vol. 7, pt. 3, 1903, p. 213).

Finally, whenever possible, a thorough microscopic examination of the rock in thin section should precede the chemical analysis. This may be of the greatest aid to the chemist in indicating the presence of unusual constituents or of more than customary amounts of certain constituents, whereby, possibly, necessary modifications in the analytical procedure may be employed without waste of time or labor.¹

If the point is raised that many of the published analyses emanating from the Survey laboratories, even my own earlier ones, are not in accord with the advocacy of completeness contained in the foregoing pages, it may be remarked that these ideas were to a considerable degree evolved during a personal experience of over 25 years in this kind of work, and that frequently the exigencies were such as to compel restriction in the examination. Where this was necessary, subsequent development in some cases showed it to be bad policy in every respect. It is better, for both the geologist and the chemist, to turn out a moderate amount of thorough work than a great deal of what may ultimately prove to be of more than doubtful utility.

2. THE CONSTITUENTS OCCURRING IN SILICATE ROCKS.

It is to the decomposition of the original igneous rocks or their magmas and their derivatives that nearly all ore bodies in the United States owe their origin by one or another process of concentration. A certain class of concentrates probably separated from magmas in the fluid state before solidification. Hence it is the natural and inevitable inference that sufficiently careful examination of these rocks would show them to contain all or nearly all the known elements, not necessarily all in a given rock, but many more than anyone has yet found.² Mechanical and analytical difficulties have thus far stood in the way of experimental proof that this is so, owing to the great scarcity of many of the elements. In exceptional cases it may be desirable to subject a given material to very exhaustive analysis, as, for instance, when searching for the origin of ore deposits. Ordinarily, however, the demands of the petrographer and geologist are satisfied with a knowledge of the quantitative relations of those constituents which can be determined

¹ See also Washington, H. S., *Chemical analysis of rocks*, 1919, pp. 6-7. The foregoing tables and accompanying remarks, including several sentences preceding the tables, have been largely taken from my paper entitled, *A plea for greater completeness in chemical rock analysis*: Jour. Am. Chem. Soc., vol. 16, 1894, pp. 90-93; Chem. News, vol. 69, 1894, p. 163. See also *Distribution and quantitative occurrence of vanadium and molybdenum in rocks of the United States*: Am. Jour. Sci., 4th ser., vol. 6, 1898, p. 209; Chem. News, vol. 78, 1898, p. 216; and Bull. U. S. Geol. Survey No. 167, 1900, p. 49.

² F. Sandberger's researches showed to what extent this is true of a large number of those elements contributing to the filling of metalliferous veins, and L. Dieulafoy by his elaborate qualitative researches showed how universal was the distribution of copper, zinc, barium, strontium, etc., in the primordial rocks.

in a limited amount of the sample—say, from 0.5 gram to 2 or occasionally 5 grams. In general the discussion relating to silicate analysis in this volume will be confined to such separations as may be required in the analysis of an igneous, metamorphic, or sedimentary rock of complex mineralogical composition, in which the majority and possibly all of the ingredients in the list given below may occur in weighable or readily discoverable quantities:

SiO_2 , TiO_2 , ZrO_2 , Al_2O_3 , Fe_2O_3 , Cr_2O_3 , V_2O_5 , FeO , MnO , NiO , CoO , MgO , CaO , SrO , BaO , ZnO , CuO , K_2O , Na_2O , Li_2O , H_2O , P_2O_5 , S^1 , SO_3 , C^2 , CO_2 , F , Cl , N .

To the above list might be added certain others, as the group of so-called rare earths, besides tin, platinum, tantalum, columbium, boron, glucinum,³ helium. Some of these occur at times in determinable amounts, though in my experience tantalum, columbium, and glucinum have not been met with. They may very well have been overlooked by reason of the absence of distinctive tests for identification. Thorium, cerium, and other rare earths are probably more common as constituents of silicate rocks than has been generally supposed. Their presence and amount can be so readily and certainly detected by the methods given in their proper place that the reason for neglecting to look for them is no longer so strong as it used to be, especially when there is microscopic or other evidence of the presence of minerals likely to contain them.

3. THE DISTRIBUTION AND OCCURRENCE OF CERTAIN MINOR CONSTITUENTS.

For the suggestion of this section and for much of its contents I am in no small degree indebted to Washington's book (Manual of the chemical analysis of rocks, 1919, pp. 17-21).

Washington says:

The increased number of analyses of igneous rocks, especially of those of unusual types, and the more frequent determination of the minor constituents, with the vast mass of data obtained by the use of the microscope, have shown that certain of the rarer elements are prone to occur in rocks of certain chemical characters. While our knowledge along this line is far from complete, a few words may be devoted to this subject, as it will often be of use to the analyst to know which elements should be especially looked for and which may safely be neglected.

Titanium.—Not long ago held to be rare, titanium is now recognized to be one of the most universally distributed elements and about tenth in actual abundance in the explored crust of the earth. So far as my experience goes, it is entirely absent from no igneous,

¹ Usually as pyrite, occasionally as lazurite, not infrequently as pyrrhotite.

² As graphite or coaly matter.

³ For probably the best method of separating even very small amounts of glucinum from iron and aluminum see Parsons, C. L., Jour. Am. Chem. Soc., vol. 28, 1906, p. 1589; Chem. News, vol. 95, 1907, p. 188.

metamorphic, or sedimentary rock of a more or less siliceous character. The recognition of this fact has been rendered possible and easy by its characteristic behavior, when in solution, toward hydrogen peroxide. Though seemingly present even in most siliceous rocks, it is most abundant in the so-called basic rocks. Its chief mineral occurrences are as rutile, octahedrite or anatase, ilmenite, titanite, and perovskite, but it is also a component in smaller amounts of many pyroxenes, hornblendes, biotites, garnets, and other ferromagnesian minerals, and is found in some magnetite and hematite. Owing to the refractory nature of some of its compounds it tends to concentrate in the residual products of decomposition of many rocks; hence its high percentage in clays as a class. It is very unusual to find titanium present in amounts that can properly be designated only as traces. In the great majority of cases its amount will not exceed 1 per cent, but it may rise to over 5 per cent.

Zirconium.—The chemically related element zirconium is likewise now known to be more widely distributed than was formerly supposed, but it is much less common than titanium, rarely making up 0.2 per cent of a rock and being usually under 0.05 per cent.

Zirconium * * * is apt to occur in granites, pegmatites, rhyolites, syenites, and in nephelite syenites, phonolites, and tinguaïtes. It is most abundant in rocks which are high in soda, such as the last three. It is rarely met with in rocks rich in lime, magnesia, and iron. Zirconium is usually found as the silicate zircon, especially in granites and syenites, but is also an ingredient of such rare minerals as eudialyte, lâvenite, and rosenbuschite.

Rare earths.—The rare earths * * * are found, so far as known, in notable amount only in rocks that are high in soda. They form part of allanite, a mineral that is rather widespread in granites, and also of monazite, mosandrite, xenotime, and other minerals of even greater rarity. They are almost always accompanied by notable amounts of zirconia. The rare earths, reckoned as $(\text{Ce}, \text{Y})_2\text{O}_3$, seldom are present in more than one-tenth of 1 per cent, but two rocks are known in which they are present to the extent of 0.4 and 0.6 per cent. Scandium has been shown to be widespread in traces.

Chromium.—Chromium is almost wholly confined to the femic [ferromagnesian] rocks, especially those which are high in magnesia and low in silica, and consequently contain abundant olivine, such as peridotite and dunite. It occurs as chromite and picotite (chrome-spinel) and in some augites, biotites, and olivines. It may occur up to one-half of 1 per cent of Cr_2O_3 .

Vanadium.—The distribution of vanadium has been covered in part by the remarks on pages 22–23. To leave out of account the well-characterized mineral vanadates, its most stable and normal form in the silicates seems to be that of trivalency, corresponding to the oxide V_2O_3 , in which form it replaces alumina and possibly ferric oxide to a very minor extent—a few hundredths of 1 per cent—in pyroxenes, hornblendes, and biotites. Hence it predominates in the less siliceous igneous rocks. As the mineral roscoelite, essen-

tially a vanadio-alumino-potassic silicate, or some other similar silicate, it is rather widely distributed as a component of certain sandstones in western Colorado and eastern Utah, sometimes in large amount.¹ It may well exist in a similar condition in clays and the ashes of coals. The conclusion being based on the above observations, it should not occur as a constituent of nonaluminous and nonferrie rock-forming minerals. As to olivine, at least, this conclusion has been found to be justified. Vanadium is also a constituent of ilmenite in titaniferous iron ores. The existence of the copper sulphovanadate, sylvanite, and the occurrence of vanadium in apparent combination with sulphur in certain peculiar carbonaceous ores of eastern Utah and Peru² indicate a possible wider range of combination in exceptional cases.

Manganese.—This element is found in ferromagnesian minerals in nearly all rocks, though as the result of their alteration it may appear sometimes, particularly on surfaces of limestones and sandstones, in a more or less peroxidized condition. Its amount will seldom exceed 0.3 per cent. I agree fully with Washington in regarding the high figures commonly reported as due to analytical error. There is no element which the average chemist is more prone to report too high, by gravimetric methods.

Nickel and cobalt.—These elements are found in the olivine of peridotite rocks and also in pyrite and pyrrhotite, hornblende, and biotite. Even in peridotites the percentage of nickel will seldom exceed 0.1 per cent, while that of cobalt rarely if ever exceeds a trace. As with manganese, the percentage of nickel has often been reported too high.

Copper.—Owing to the extreme precautions necessary to exclude its introduction from utensils and reagents during analysis, there is less positive information regarding the distribution of copper than of some other elements which do not exceed it in amount. Nevertheless, there is reason to believe that it is almost if not quite as universally distributed as most of the other minor constituents. Its particular home appears to be in diabase, gabbro, amphibolite, and other basic rocks with pyroxene and amphibole. J. B. Harrison, in a report (1906) to the Science and Agriculture Department of British Guiana, shows its occurrence in hundredths of 1 per cent in many igneous rocks of that colony. So far as my experience goes, it can be found almost invariably, if looked for, in the rock analyses carried out in the Survey laboratory. But for the reason above given it is seldom

¹ Hillebrand, W. F., and Ransome, F. L., *Am. Jour. Sci.*, 4th ser., vol. 10, 1900, p. 120; *Bull. U. S. Geol. Survey* No. 262, 1905, p. 9.

² As to the Peruvian occurrence see Hewett, *Foster, Eng. and Min. Jour.*, vol. 82, 1906, p. 385; Bravo, José J., *Bol. Soc. Ing. (Lima)*, vol. 8, 1906, p. 171; Hillebrand, W. F., *Am. Jour. Sci.*, 4th ser., vol. 24, 1907, p. 141; *Jour. Am. Chem. Soc.*, vol. 29, 1907, p. 1019.

reported unless extra precautions have been taken to prevent its extraneous entry into the analysis.

Barium and strontium.—Feldspathic rocks are those most likely to carry barium and strontium, the former almost always in excess of the latter.

There is some evidence that barium is apt to be most abundant in rocks which are high in potash. Barium occurs in the feldspars, especially orthoclase, as the celsian molecule, in the rare hyalophane, in some zeolites, as well as in a few biotites and muscovites. We can at present form no definite conclusion as to the character of the rocks most likely to carry strontium, and more analytical data on this point would be of interest.

Barium has been found in a few peculiar rocks in excess of 1 per cent, in terms of the oxide, but in the greater part of the silicate rocks of the United States its percentage is well below 0.2. Strontium has been found as high as 0.3 to 0.4 per cent, but generally there is little more than a trace of it.

Lithium.—Although one of the most universally distributed of the elements, lithium is almost never found in rocks in more than spectroscopic traces. Aside from the lithium minerals lepidolite and spodumene, it is found in the alkali feldspars, in muscovite, beryl, and other minerals. According to Washington, there is reason for the belief that it is especially prone to occur in highly sodic rocks.

Phosphorus.—This element is found in greatest abundance in the more basic igneous and metamorphic rocks and is practically never entirely absent. It affects especially those rocks "which are high in lime and iron rather than in magnesia." Its chief mineral occurrence is in apatite, though it may be found in xenotime and monazite. While the percentage is usually well under 1, it may considerably exceed this figure.

Sulphur.—Aqueous extraction of a powdered rock will in many cases remove traces of sulphur and chlorine. These are to be regarded almost invariably rather as derived from infiltrating waters than as products of decomposition of the constituents of the rock itself. Essential rock-forming minerals containing sulphur in the oxidized condition are limited to haüynite and noselite, minerals which are found chiefly in the more basic rocks, and especially those high in soda. In the sulphide condition the element is of very wide distribution, both as pyrite and pyrrhotite, less often as chalcopyrite and possibly other sulphides, also in the mineral lazurite, and here too in greater abundance in the basic rocks. It is a very common error of most chemists to report the sulphur in silicate and carbonate rocks, clays, etc., as SO_3 instead of S. Now and then it may occur in both states, but much more often only in the sulphide condition.

Chlorine.—Washington says:

Chlorine is present most abundantly in rocks which are high in soda, and especially when so low in silica that nephelite is present, though it is also found sometimes in nephelite-free rocks and in a few cases in quartz-bearing ones. It is an essential component of sodalite and noselite and is also present in scapolite and in a few apatites.

Its amount when present rarely exceeds 0.2 or 0.3 per cent. When seeking for the chlorine of these minerals it is always well to extract the powder first with cold water. (See preceding paragraph.) It is to be remembered that fluid inclusions in minerals sometimes contain sodium chloride, which would be largely extracted from the powder by water.

Fluorine.—Washington says:

Fluorine as a component of apatite, biotite, etc., seems to have no special preference as to magma, though, on the whole, it is found more frequently in silicic than in femic [ferromagnesian] rocks. It is, however, most apt to be met with as fluorite and some other rare fluorine-bearing minerals in rocks that contain nephelite, as foyaites and tinguaites. It is an essential constituent of fluorite and most apatite, and as an integral part of the last mineral is almost universally present. It also occurs in small amounts in biotites and other micas, in some hornblende and augite, as well as in tourmaline, topaz, chondrodite, etc.

When determined it is usually reported in amounts under 0.1 per cent, but freedom of the weighed calcium fluoride from contamination being assumed, the reported amount is invariably too low because of the inaccuracy of the method for its separation. (See 25. B. a. γ , p. 225.)

Other minor constituents.—Washington says:

Glucinum, as a component of beryl and some other very rare minerals, is most frequent in granites, pegmatites, and quartzose gneisses; it seems to be most at home in sodic rocks. There is reason to think that the high alumina sometimes reported for these rocks may be in part glucina, which has not been separated from the alumina, and due to the presence of unidentified beryl. * * * Tin, as the oxide cassiterite, is confined to the highly silicic rocks, granites, and pegmatites, and its presence is due generally to pneumatolytic processes. It also may occur in traces in ilmenite, micas, and feldspars. Thorium would seem to be more abundant in highly sodic rocks, and the same is also apparently true of radium and the radioactive elements. Molybdenum, tungsten, and uranium are almost exclusively confined to the very siliceous rocks. Zinc has been met with in granite, as well as in basic rocks, but no generalization in regard to it is possible as yet [nor in regard to lead, which can often be found by using considerable amounts of rock material, as in some of the rocks of Leadville, Colo., and in those of British Guiana.—W. F. H.]. Platinum is found almost exclusively in peridotites, but is occasionally met with in connection with gabbros. Boron, usually as a constituent of tourmaline, is most apt to occur in highly siliceous rocks.

Boron is also common in many contact-metamorphic schists. Gold and silver have been found repeatedly. According to Harrison,¹

¹ Rept. Sci. and Agr. Dept. British Guiana, 1906.

some of the rocks of British Guiana contain gold enough to account for the commercially valuable deposits in residual soils resulting from the rock decomposition. Tantalum and columbium occur in some granites and pegmatites but have never been reported in percentages in rock analysis, so far as known to me.

4. SUMMATION OF ANALYTICAL RESULTS AND LIMITS OF ALLOWABLE ERROR.

As is well known, a complete silicate-rock analysis which foots up less than 100 per cent is generally less satisfactory than one which shows a summation somewhat in excess of 100. This is due to several causes. Nearly all reagents, however carefully purified, still contain or extract from the vessels used traces of impurities, which are eventually weighed in part with the constituents of the rock. The dust entering an analysis from first to last is considerable, washings of precipitates may be incomplete, and if large filters are used for small precipitates the former may easily be insufficiently washed.

Given the purest obtainable reagents, an ample supply of platinum, facilities for working, and a reasonably clean laboratory, there is usually little excuse for failure on the part of a competent chemist to reach a summation within the limits 99.75 and 100.50. Failure to attain 100 per cent in several of a series of analyses of similar nature should be the strongest evidence that something has been overlooked. Excess above 100.5 per cent should be good ground for repeating portions of the analysis in order to ascertain where the error lies, for it is not proper to assume that the excess is distributed over all determined constituents. It is quite as likely—in fact, more than likely—to affect a single determination and one which may be of importance in a critical study of the rock from the petrographic side.

Washington would extend the allowable limits above given to 99.50 and 100.75. If the analysis has to be made in other vessels than those of platinum a higher limit than 100.50 is certainly called for, but it is extremely doubtful if a lower one than 99.75 should be accepted, for, as has been said, there is a tendency toward too high results in any case, and a summation of less than 99.75 with vessels other than platinum would be indicative of rather gross error on the part of the analyst.

As to the allowable variation in duplicate determinations of the same constituent no rigid rules can be laid down. Washington has proposed the following,¹ with which the independent experimental values of Dittrich² are in substantial agreement: For SiO_2 and others which amount to 30 per cent and over, from 0.2 to 0.3 per cent; for Al_2O_3 and others which amount to from 10 to 30 per cent, 0.1

¹ Manual of the chemical analysis of rocks, 1913, p. 127.

² Neues Jahrb., 1903, vol. 2, p. 69.

to 0.2 per cent; for constituents which amount to from 1 to 10 per cent, 0.05 to 0.1 per cent. These percentages are in terms of the whole rock and not of the particular constituent.

While it is desirable sometimes, and for the beginner imperative, to make duplicate determinations, agreement is not to be taken as proof that the results are correct unless they have been arrived at by different methods.

Too great stress can not be laid upon the importance, especially for the analyst of limited experience, of consistently testing most of his final precipitates and filtrates as carefully as possible in order to be sure, on the one hand, that the substances reported by a given name are wholly such and, on the other, that all is reported. In no other way can an analyst so soon acquire the needed confidence in himself and his methods.

5. STATEMENT OF ANALYSES.

For many years it was the practice in the Survey laboratory to tabulate the constituents of a rock somewhat in the order of their determination, beginning with SiO_2 as the chief constituent and grouping together all chemically related oxides, as shown, for instance, on page 21.

From a strictly scientific point of view a chemical classification founded on a separation into basic and acidic atoms or radicals would be more satisfactory, but until we learn to find out what silicic radicals are present and in what relative amounts, also how much free silica there may be, it is useless to think of employing the arrangement so valuable in stating water analyses.

Petrographers now demand, with considerable reason, an arrangement "which shall bring the essential chemical features—both the percentage figures and the molecular ratios—prominently and compactly before the eye, so that the general chemical character and the relations of the various constituents may be seen at a glance."¹

In accordance with this demand it is now the Survey practice to follow pretty closely the arrangement proposed by Pirsson and later strongly advocated by Washington,¹ namely:

SiO_2 , Al_2O_3 , Fe_2O_3 , FeO , MgO , CaO , Na_2O , K_2O , H_2O (above $105-110^\circ$), H_2O (below $105-110^\circ$), CO_2 , TiO_2 , ZrO_2 , P_2O_5 , SO_3 , Cl , F , S (FeS_2), Cr_2O_3 , V_2O_5 , NiO , CoO , CuO , MnO , SrO , BaO , Li_2O , C , NH_3 .

By this arrangement the nine constituents which in the great majority of cases determine the character of the rock are placed at the head of the list, thus facilitating greatly the comparison of dif-

¹ Washington, H. S., The statement of rock analyses; Am. Jour. Sci., 4th ser., vol. 10, 1900, p. 61.

ferent analyses similarly arranged, especially when, as Washington recommends, the molecular ratios are calculated for these leading constituents and placed immediately after the corresponding oxides. The order of the remaining members is determined somewhat by the following considerations: CO_2 is placed next after H_2O , for these two are generally a measure of the alteration the rock may have undergone. TiO_2 and ZrO_2 naturally follow CO_2 on chemical grounds, and SO_3 and Cl , being common constituents of the sodalite group, are conveniently placed together.

It may be said with regard to the use of the word "trace" that the amount of a constituent thus indicated is supposed to be below the limit of quantitative determination in the amount of the sample taken for analysis. It should in general, for analyses laying claim to completeness and accuracy, be supposed to indicate less than 0.02 or even 0.01 per cent.

6. TIME NEEDED FOR MAKING AN ANALYSIS.

The question has often been put, "How long does it take to complete an analysis of this kind?" This will depend, of course, on the mineral complexity of the sample and on the personal factor of the individual worker. If there is a competent assistant to do the grinding, and specific-gravity determinations are not required, it is quite possible after long experience for a quick worker to learn to so economize every moment of time in a working day of seven hours, with an abundance of platinum utensils and continuous use of air and water or steam baths through the night, as to finish every three days, after the completion of the first analysis, barring accidents and delays, one of a series of rocks of generally similar character, each containing from eighteen to twenty quantitatively determinable constituents, excluding, for instance, fluorine, carbon as such, nitrogen,

FIGURE 1.—Platinum-tipped crucible tongs. The parts A, B, also of heavy platinum, are hollow, to serve as sockets for the cheaper metal of the handles.

metals of the hydrogen sulphide group, and cobalt. But such an output of work implies an unusual freedom from those occasional setbacks to which every chemist is exposed.

7. USEFUL APPLIANCES AND APPARATUS.

In connection with the foregoing remarks it is in place to mention a few aids to the chemist which are in constant use in the Survey laboratory and have come to be well-nigh indispensable. None is novel in principle and all are in use elsewhere, but some are not so commonly known as they deserve to be, hence this allusion to them. Certain cheap and simple forms of colorimeters have been found very useful, and as they are adapted to the determination of a variety of substances their description finds most appropriate place here.

A. CRUCIBLE TONGS.

Figure 1 represents a form of platinum-tipped crucible tongs devised by A. A. Blair many years ago. With them a crucible can be securely grasped and brought into any desired position while still hot. To the contents, if in fusion over the blast flame, can be imparted the rotatory motion so often desirable. Above all, the cover need not be in the slightest degree displaced, as when using the common form of platinum-tipped tongs.

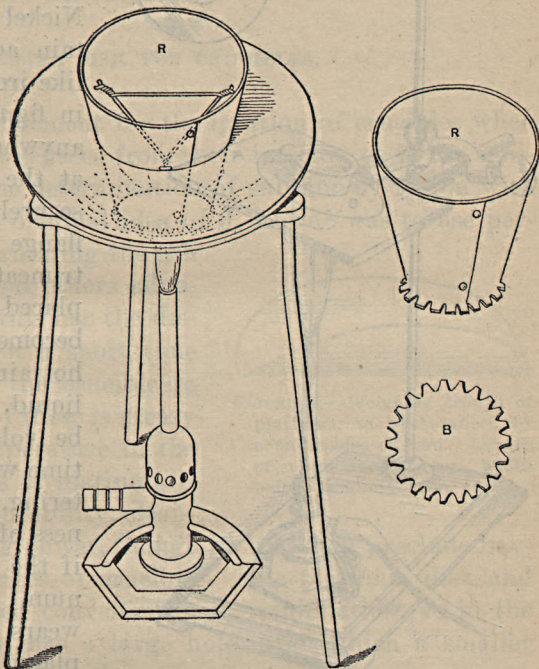


FIGURE 2.—Radiator for rapid and safe evaporation. R is of sheet iron or aluminum, also nickel (Jannasch). A convenient height is 7 cm., width at top 7 cm. and at bottom 5 cm. The base, B, may be of iron, nickel, or platinum, but not aluminum, which will not stand the temperature of the direct flame. Platinum is most satisfactory by reason of its long life and radiating power. The manner of attaching B to R is by turning the cogs of B up and over those of R. Evaporation may be greatly hastened when desired by placing upon R a cast-iron ring with its opening somewhat larger than the mouth of the crucible.

B. RADIATORS FOR VOLATILIZING LIQUIDS AND SOLIDS.

Figure 2 represents a very useful adjunct to the work table and especially to the draft cupboard, whereby the liquid contents of crucibles can be evaporated speedily at almost any desired temperature

and the dehydration of many solids effected much more safely than on an iron plate or sand bath. I do not recall who originated this form

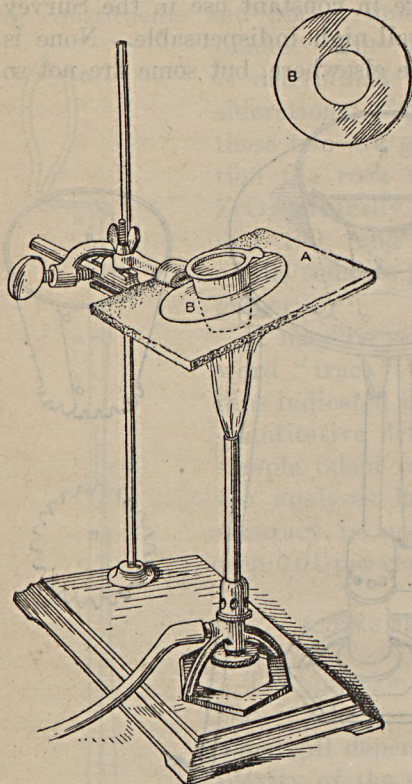


FIGURE 3.—Device for excluding flame gases from the interior of crucibles during ignition. A, Asbestos board; B, stiff platinum foil of size suitable to the crucible used and having an opening to admit the crucible to about two-thirds of its depth. This disk may be used alone upon the ring of an ordinary stand and in horizontal position, or, preferably as shown in the figure, in combination with the asbestos board, in which is an opening considerably larger than the crucible. The combination should then be given the inclined position shown, so as to allow the products of combustion to flow to one side without the possibility of their enveloping the mouth of the crucible. In the lack of platinum a perforated asbestos board alone will yield fair service with a blast, but not as a rule with an ordinary burner.

The outer dish may be of iron, direct contact between it and the inner dish being prevented by wisps of asbestos overlapping its edge, but

of air bath, but it has been in use for over 30 years and is identical in principle with the "Nickel-becher" of Jannasch. Nickel undoubtedly has a certain advantage in not rusting like iron, but the form depicted in figure 2 can be made easily anywhere of sheet iron riveted at the joint, the bottom being securely held by a notched flange at the extremity of the truncated cone. A crucible placed on the platinum triangle becomes heated uniformly by hot air, and large quantities of liquid, even sulphuric acid, can be volatilized thus in a short time without ebullition or spattering. The life and effectiveness of this appliance is greater if the bottom is of sheet platinum, but if an iron bottom wears out it can usually be replaced one or more times before the sides fail. A coating of aluminum paint on the sides adds to their life.

By an extension of the principle illustrated in figure 2 very considerable amounts of ammonium salts and other easily volatile solids may be driven off from platinum dishes with little danger of loss by spattering and none by overheating. The dish containing the dry or nearly dry matter is placed in another of such size that the bottom of the inner dish is at some distance from that of the outer.

the excellent conductivity and radiation of platinum recommends it above anything else. Aluminum will not stand the application of a full flame. If the contents of the dish are moist at first, a low flame will soon dry them, when the heat may be increased at will and the operation allowed to proceed without supervision. A sand bath may be substituted sometimes for the radiator.

C. PERFORATED DISK FOR CRUCIBLES.

Figure 3 shows an arrangement for the ignition of crucibles when it is desired to exclude flame gases from their interior, as in the ignition of ferric oxide and the determination of sulphur by fusion with an alkali carbonate. The original idea of J. Löwe¹ was to use perforated clay disks in determining the ash of coals. Later, Lunge and others advocated asbestos board, but this has the disadvantage that it lasts but a short time and the fibers adhere to the crucible to some extent. By neither of these is it easy to attain a very high temperature in the crucible. Therefore a disk of platinum is preferable because of its durability, cleanliness, and high conducting power, though its cost may preclude having a set to fit different sizes of crucibles. The platinum disk and asbestos board may be used conveniently in combination, as in the figure. The asbestos then has a large hole, over which a smaller perforated disk of platinum is laid.

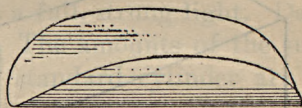


FIGURE 4.—Weighing trough of platinum, to be balanced by counterpoise of lead. Length of trough about $7\frac{1}{2}$ cm.; width before bending, 5 cm.

D. WEIGHING SCOOP OR TROUGH.

Figure 4 represents a most convenient receptacle for the sample that is being weighed on the balance. It is made of platinum and is counterpoised by a leaden weight. It has the advantage over a watch glass in that its shape permits ready introduction of its contents into narrow-mouthed receptacles when desired.

E. COLORIMETERS.

a. FIRST SURVEY FORM.

The Survey form of colorimeter shown in figure 5 consists of two glass reservoirs and a darkened box. The glasses, G, may be of square or oblong section, 8 to 12 cm. high and 3 to $3\frac{1}{2}$ cm. inside measurement between those sides through which the liquid is to be

¹ Zeitschr. anal. Chemie, vol. 20, 1881, p. 224.

observed.¹ These sides should, of course, be exactly parallel; the others need not be but should be blackened externally. In order to exclude further the effect of side light, it is very convenient to have a simple light box, B, that can be easily held in the hand, stained black inside and out and with one end closed by a piece of ground glass, W, the other being open. For a space equal to the width of the glasses the cover is removed at the top next the glass end to permit the insertion of the glasses side by side in such a way that no

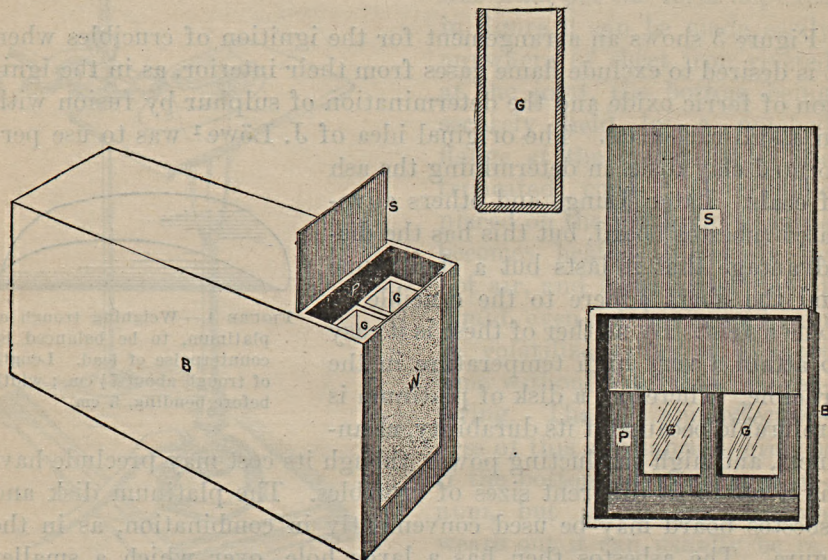


FIGURE 5.—First Survey form of apparatus for colorimetric determinations, different aspects. G, One of two glasses of square or rectangular section, 8 to 12 cm. high and 3 to 3½ cm. inside measurement between those sides through which the liquid is to be observed. The other sides are blackened on the outside. B, Rectangular box about 35 cm. long and 12 cm. square, stained black inside and out, one end closed by a ground-glass window, W, the other open, and a portion of the top removed. P, Blackened partition, with openings corresponding to the interior dimensions of the glasses when in position. S, Blackened cardboard shutter sliding stiffly up and down back of the partition.

light shall penetrate around their sides or between them. Immediately back of the glasses is a partition, P, with openings of appropriate size cut in it. A stiffly sliding black cardboard shutter S, is movable up and down immediately back of the partition, so that all light can be cut off except that which comes through the liquid. The

¹ The allowable error in distance between the corresponding pairs of sides of the two glasses should never exceed 1 per cent. Unfortunately there has been a disinclination on the part of dealers in this country to furnish glasses fulfilling this requirement, and held together by a durable cement which shall be proof against dilute sulphuric acid and alkali, though some have been obtained through Messrs. Elmer & Amend, of New York City. Canada balsam answers well for a time, but sooner or later it cracks, leaks then appear, and the sides soon drop off. However, it is but a simple matter to cement them on again. But the use of Canada balsam is precluded with alkaline solutions, and hence for the chromium determination, because the solution at once becomes turbid.

ground-glass window, W, sliding up and down in slots, affords a much more uniform illumination than can be had without it.

Precautions of this kind are necessary if accurate results are to be counted on. Except for mere traces, this combination of glasses and darkened box insures greater accuracy and rapidity of work than Nessler tubes and is likewise preferable, so far as my experience goes, to expensive instruments like the colorimeter of Soleil-Duboscq.

The manner of using the colorimeter is as follows: Any suitable amount of the standard solution, which is purposely made stronger than the solution to be tested, is placed in one of the glasses and an indefinite part or the whole of the test solution in the other. Water is then added from a burette to the standard until there is no distinction as to color. Perfect mixture is brought about by a glass rod flattened at one end. In making the color comparison the box is best held close to a window, so as to get a full, strong light. Daylight is far preferable to artificial light. The amounts of the substance to be determined and that in the standard cylinder are of course proportional to the volumes of the solutions.

D. SECOND SURVEY FORM (STEIGER'S).

The colorimeter shown in figure 6 was devised by George Steiger. Though more elaborate in its construction than the one just described, it permits making any number of readings with the same standard solution and has given Steiger excellent service. Its construction and use are thus described by him.¹

Instruments using the principle upon which this one is based—the ratio of the thickness of the liquid through, and not the actual dilution to equal concentrations—are not applicable to all colorimetric determinations. It will be found, in comparing such a solution as is used in the colorimetric determination of manganese and some other substances, that there is a change not only of the intensity of the color, but also of the color itself, making it impossible to find a point at which two solutions of different concentrations will have the same depth of tint. In some other cases, as for instance, the yellow color of the higher titanium salts, this principle gives perfect satisfaction.

The instrument to be described consists of two wooden boxes, the interior portions of which are finished in dead black. In fig. 6 (a), AA is a piece of finely ground glass, and this should be illuminated with the full light of the sky. B is a mirror mounted to swing so that light may be thrown perpendicularly through the hole C.

The second portion of the apparatus consists of a box, as shown in fig. 6 (b), made with two parallel grooves in the bottom, in which the two glass cells CC can be moved back and forth, and the hole E, which admits light reflected by the mirror B of fig. 6 (a). These cells are about 15 cm. long, 2.5 cm. wide, and 5 cm. deep. On the bottom of each cell and near the outside edge is engraved a scale, a convenient unit for which is the millimeter. FF are glass tubes with mirrors, GG, attached to the lower ends at an angle

¹ Jour. Am. Chem. Soc., vol. 30, 1908, p. 215.

of 45° . These tubes may be lifted up when it is desired to remove the cells; they may also be removed entirely from the clips RR for cleaning purposes, but they should be pushed down when in use so that the lower edges of the mirrors touch the bottoms of the cells. When ready for use this box is placed in the space marked DD, fig. 6 (a). Care should be taken to place the mirrors at an exact angle of 45° .

Under these conditions, in each cell, all light coming through the bottom of the cell and reflected through the end K will go through the same thickness of liquid, and if the mirror were a reflecting surface coming in direct contact with the liquid this distance would be represented by the line OP, fig. 6 (c).

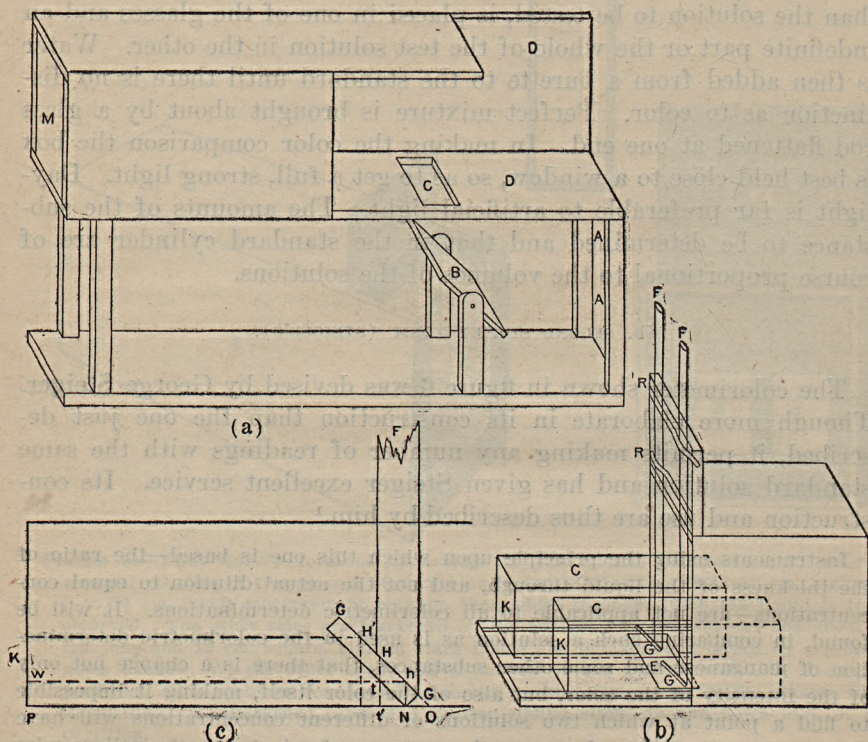


FIGURE 6.—Steiger's colorimeter (second Survey form).

There is a small error here, due to the converging of the rays to the eye; this is so slight, however, as not to cause any perceptible uneven illumination.

The mirrors being made of ordinary looking glass, the reflecting surface will be the upper side GHG, fig. 6 (c), and the light must go through the glass of the mirror before striking the reflecting surface, and the same on leaving. The distance which the light travels through the glass of the mirror will be represented by twice the length of the hypotenuse of an isosceles right-angle triangle, the equal sides of which are each equal to the thickness of the glass, and must be deducted from the length OP.

A ray of light entering the glass at the point marked N will travel to *h* and then be reflected to *t*. From *t* to *w* it will go through the colorimetric solution, and this distance is therefore the length to be measured. A point, H, is marked on the mirror near the outer edge, so that it may be seen in the same line of

vision as the scale on the bottom of the cell, and perpendicularly above t . In looking through the end K, this mark will be recorded at the point t' directly below it on the scale, and $t'P$ being the same as tw , the distance desired can be read off. The position of the point H is determined by measuring off, on the back of the mirror, a distance from the lower edge equivalent to three times the thickness of the glass. It may be convenient, if thin looking-glass has been used, to have this point farther up on the mirror (H'), in order that it may be seen more plainly, but if so moved an addition must be made to the observed reading equivalent to one of the sides adjacent to the right angle of an isosceles right-angle triangle, the hypotenuse of which is equal to the distance this point has been removed from H. It is convenient in making the graduation on the cell to allow for this correction. The reading can then be made directly.

Glass cells to answer the purpose may be had of any of the large supply houses, but not graduated; the graduation must be done in the laboratory. The supports FF can be made of rather heavy walled glass tubing, about 1 cm. outside diameter.

The mirrors are made of a good grade of looking glass, the lower and top edges blackened, and cemented to the ground ends of the glass tubes with Canada balsam, after which the backs are coated with paraffin. Paraffin answers well as a coating for a large number of colorimetric solutions. In case a liquid is to be used which attacks paraffin, a substitute must be employed which is unaffected by the liquid in question. It will be found necessary to replace the mirrors from time to time, as it is not possible to so protect the silvered surfaces as to prevent the gradual eating in from the edges by the various solutions used.

The comparison is made by pouring a solution of known strength into one of the cells. The unknown solution made up to a definite volume is put into the other. The left-hand cell is then placed at a convenient point, which should be determined by the depth of color of the solution it contains. The right-hand cell is then moved back and forth till, on looking in the end M of the apparatus, fig. 6 (a), the two mirrors appear to be of the same shade.

The strengths of the two colorimetric solutions being inversely proportional to the thickness of the liquids looked through, by substituting in the following equation the amount of the material to be determined may be found.

Let R equal the reading of the cell containing the known solution with a concentration C, and r the reading of the cell containing the unknown solution, which has a concentration c , then

$$c = \frac{RC}{r}$$

C. SCHREINER'S FORM.

Oswald Schreiner, of the United States Department of Agriculture,* devised a colorimeter (fig. 7),¹ which has done good service in colorimetric work on phosphates, etc. Its description, personally communicated by Dr. Schreiner, is as follows:

The colorimeter in its simplest form consists essentially of graduated glass tubes B, containing the standard and the unknown colorimetric solution, the column of the liquid in both tubes being changed by means of two smaller im-

* Jour. Am. Chem. Soc., vol. 27, 1905, p. 1192.

mersion tubes A, also of glass. The upper ends of the tubes A are mounted in blocks of wood which fit into grooves on the body of the colorimeter. This permits the ready removal of the tubes from the colorimeter for cleaning when the liquids are changed. The graduated tubes B are supported by a block of wood about midway of the camera and are held in place by brass springs or clamps C, the tension of which can be regulated to suit the diameter of the tube, so as

to allow it to be moved freely up or down by hand and yet be firmly held in position when the setting is made. It will be noticed from the figure that the glass tubes diverge slightly. This has been found of advantage, as it allows the operator to look down the center of both immersion tubes, as well as to bring the upper parts of the tubes, and consequently the images, closer together. The openings to the immersion tubes can be covered by means of a microscope slide to prevent dust from falling into the tubes. The tubes are illuminated from the reflector D, below, which carries a white sheet of cardboard or opal glass, and after passing through the tubes the light is reflected by a mirror, E, in the upper part of the instrument to the eye of the observer at F. The dimensions of the camera are about 70 by 32 by 16 cm. Standard glass slides may be inserted at G below one of the immersion tubes in place of the tube containing the standard solution, the immersion tube being retained so as to give similar images when viewed from above.

The measuring colorimeter tubes, B, are 25 cm. long, with inside diameter as nearly as practicable 27 mm.; in no case less than 25 mm. and not greater than 29 mm. The glass should be colorless and the bottoms well ground and polished, with internal surfaces of the bottoms plane, in no case appreciably convex or concave. The bottoms must be ground down sufficiently

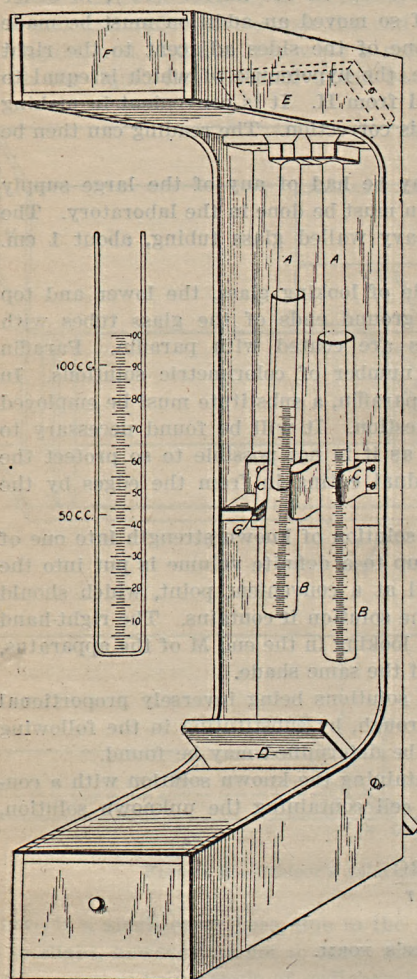


FIGURE 7.—Schreiner's colorimeter.

to make the ground surfaces a little larger than the internal diameters of the tubes; each of the tubes is provided with an etched scale of one hundred 2-mm. divisions. The scale begins at the level of the inner surface at the bottom, the length of the marks being 6 mm. and every fifth mark 12 mm., and every tenth mark numbered on the right side, 10, 20, 30, etc., beginning at the bottom. On the reverse side of each measuring tube may be etched two capacity marks, if desired, one for 50 cm.³, the other for 100 cm.³.

The smaller tubes are likewise 25 cm. long, with outside diameter not greater than 20 mm. and not less than 18 mm., with the thickness of the glass the same in all the tubes. The bottoms of these tubes must be carefully ground and polished and the inside of the bottom never sensibly convex or concave. They must be of colorless glass, with the bottoms so ground that the diameter of the ground portion exceeds the internal diameter of the tube. These tubes are to be provided with neither scale nor capacity marks.

The standard colorimeter solution is poured into one of the graduated tubes and put into place in the camera together with the immersion tube. The unknown colorimetric solution, made up to definite volume, is put into the other graduated tube and similarly placed in the instrument. The tube containing the solution of unknown strength is set at a convenient height, say fifty scale divisions, and the other tube containing the standard moved up or down, the operator watching the effect on the image in the mirror through the opening in the front of the camera. By moving the tube so that the image is alternately weaker or stronger than the standard, the setting can be accurately and quickly made. When both images show the same intensity of color, the setting is read by noting the division mark on the graduated tube opposite the ground bottom of the immersion tube. This reading will give the height of column of the standard which exactly corresponds with the intensity of color of the column of the unknown solution. It follows that the strengths of these two colorimetric solutions are inversely as the heights of the columns—that is, as the readings on the two tubes. If R is the reading of the standard solution of strength C , and r is the reading of the colorimetric solution of unknown strength c , then
$$= \frac{R}{r} C.$$
 The same formula, of course, applies when the standard is fixed and the unknown solution moved up or down until the images are of equal intensity.

8. PRELIMINARY QUALITATIVE ANALYSIS.

A complete qualitative analysis of a rock preceding the quantitative examination is in most cases a sheer waste of time. A few constituents may now and then be specially looked for, but in general time is saved by assuming the presence of most of them and proceeding on that assumption in the quantitative analysis.

This statement must not be misinterpreted, as it has been, so as to convey the impression that qualitative analysis receives little consideration in the chemical work of the Survey. For ores, mineral species, waters, etc., it is indispensable, as also in the testing of precipitates and filtrates during the course of quantitative analysis.

The student of qualitative analysis will find in papers by A. A. Noyes, W. C. Bray, and E. B. Spear¹ a vast fund of information, such as is to be had nowhere else, relating not only to the making of separations, but, and this is often of greater importance, to the completeness of these separations and to the possible limits of detection. The scope of these papers is less restricted than their titles might be thought to imply, for such elements as glucinum, uranium, vanadium, titanium, zirconium, and thorium are included.

¹ Jour. Am. Chem. Soc., vol. 28, 1907, p. 137; vol. 30, 1908, p. 481; vol. 31, 1909, p. 611; Chem. News, vol. 95, 1907, pp. 89, etc.; vol. 98, 1908, pp. 6, etc.

9. QUALITY OF APPARATUS AND REAGENTS.

Unquestionably the greatest hindrance to good work in otherwise well-equipped laboratories is the difficulty in obtaining satisfactory reagents and apparatus. This fact became apparent early to the Survey chemists, and it is due mainly to their strenuous complaints and initiative that the movement in favor of better quality arose.

A. GLASSWARE AND PORCELAIN.

Much of the glassware on the market was until recently of a very inferior grade, but the quality of the American glassware is now very much improved. It appears that several American manufacturers are turning out flasks and beakers that are equal or even superior to the Jena ware. The composition of a number of brands is given in the table below.¹

Analyses of chemical glassware.

	Kavalier beaker.	M. E. G. Co. beaker.	Pyrex beaker.	Jena beaker.	Jena flask.	Nonsol beaker.	Fry beaker.	Libbey beaker.
Al ₂ O ₃14	1.0	2.0	4.2	4.2	2.5	2.7	2.1
Fe ₂ O ₃03	.35	.25	.25	.27	.23	.22	.44
ZnO.....		5.6		10.9	10.9	7.8	3.6	
PbO.....								1.0
MnO.....	.02	.02	.01	.01	.01	.01	.03	.03
CaO.....	8.7	.66	.29	.63	.56	.79	2.6	.42
MgO.....	.17	4.3	.06	.21	.25	3.4	2.6	.08
Na ₂ O.....	7.1	10.8	4.4	7.5	7.8	10.9	9.8	8.2
K ₂ O.....	7.9	.30	.20	.37	.31	.30	1.5	.67
SiO ₂	75.9	73.0	80.5	64.7	64.7	67.3	68.6	75.9
B ₂ O ₃		3.6	11.8	10.9	10.6	6.2	8.1	10.8
P ₂ O ₅08							
SO ₃20	.02						
As ₂ O ₅	Trace.	.02	.70	.14	.19	Trace.	.18	.36
Sb ₂ O ₃60				.62		
	100.29	100.27	100.21	99.81	99.79	100.05	99.93	100.00

Selenium and fluorine were not found, but lithium was detected spectroscopically by Paul W. Merrill in all samples.

Comparative tests of a number of brands of porcelain dishes and crucibles have been made by C. E. Waters.² Two of these were of American origin. It appears that there was little choice between the five brands tested with respect to their resistance to reagents. A serious defect of the American porcelains, and also of one of the foreign brands, was the cracking of the glaze when the hot vessel was picked up with tongs. Tests made later on one of the American brands (Coors) showed an improvement in this respect.

¹ Walker, P. H., and Smither, F. W., Tech. Paper Bur. Standards No. 107, 1918; Jour. Ind. Eng. Chem., vol. 9, 1917, p. 1090.

² Tech. Paper Bur. Standards No. 105, 1917.

J. W. Mellor¹ has discussed at some length and most pertinently the action of reagents on glass and porcelain. His discussion forms the basis for the following remarks.

The action of different solutions on glass is far more vigorous than on porcelain, but some types of glass resist better than porcelain with an unsuitable glaze. It is, therefore, bad on principle to allow filtrates, etc., to lie any length of time in porcelain or glass vessels—particularly the latter. In some cases the contamination from the glass may be serious * * *. It is unfortunate that the impurities introduced from the glass or porcelain vessels are those very constituents which have to be specially determined.

The choice of the particular kind of glass to use is therefore sometimes of interest. For instance, glasses containing zinc should not be used when zinc is to be determined, for alkaline solutions extract perceptible amounts of zinc from such glasses. Again, the use of the boro-silicate glasses is counterindicated when boron is to be determined.

Mellor gives the following rules to be observed:

(1) If possible, do not allow the solutions to stand in glass or porcelain vessels for any length of time, particularly in glass. (2) If the work be interrupted, so that the solutions must stand over, if there be no other objection, acidify the alkaline solutions before they are placed on the side. (3) If solutions must stand over, it is better to use good porcelain than glass vessels. (4) A resistant glass should be used for general work in place of the more soluble types of glass. (5) For exact work a blank experiment should be made, using nothing but the regulation reagents in similar quantities, and under conditions similar to those actually employed in the analysis proper. This plan not only corrects impurities in the reagents, but it also enables us to practically eliminate the sources of error now under discussion. (6) Precipitations made in alkaline solutions which have stood for some time in glass vessels are almost certain to be contaminated with silica, and in exact work a correction must be made. (7) Remember that solutions of reagents are usually kept in glass vessels. Such solutions may accordingly be contaminated with silica, etc.

B. PLATINUM AND SUBSTITUTES.

a. PLATINUM.

Practically all platinum ware contains some iridium, or copper, or copper and rhodium, added for hardening effect. Possibly certain ware carries rhodium only as an addition. The volatility loss occasioned by strong heating (above 1,100°) of some ware is due mainly to its iridium content. Therefore, the lower the iridium content is, consistent with requisite stiffness, the better.

Some years ago iron was found in large amounts in shipments of platinum ware fresh from the factory, and its presence must still be guarded against, although the quality of American-made ware has

¹ A treatise on quantitative inorganic analysis, with special reference to the analysis of clays, silicates, and related minerals, London, Charles Griffin & Co. (Ltd.), 1913.

improved very much since then in this respect. Considerable amounts of iron can be detected readily by heating the ware to low redness, best in a muffle furnace. The surface shows then a dark or even reddish color, due to oxide of iron. Proof of the presence of iron is afforded by digesting the heated ware in hydrochloric acid. A yellow color of the acid indicates iron, and further proof is furnished by a qualitative chemical test. It is seldom that a trace of iron can not be found in this way, even though the original metal may have been entirely free from it. Iron is taken up very readily by platinum from the rolls or tools used in preparing the ware, and such iron is superficially held. If so held it can be extracted for the most part by successive heatings and extractions of the ware until no more iron is found.

Sometimes, after ignition, a calcium content can be detected by the alkaline reaction imparted to a strip of moist litmus paper pressed upon the surface. Such reaction appears only in spots.

Platinum vessels should not be heated strongly in contact with metal of any kind except platinum.

D. SUBSTITUTES FOR PLATINUM.

If the restrictions imposed by its relatively low melting point are taken into account, gold may be used for many operations in place of platinum, especially in the form of dishes, which seldom have to be exposed to temperatures approaching the melting point of the metal.

Substitutes that have been put upon the market under the trade names "palau" and "rhotanium" are alloys of gold and palladium. They may be used for many operations, with certain restrictions. Chief of these is that arising from the relatively strong action upon them of nitric acid. Their low melting point as compared with platinum is not an important defect, for it is considerably higher than that of gold alone. Nevertheless, a few reports have been received at the Bureau of Standards which indicate that these substitutes do not stand up as well in service as platinum. How much the failures may have been due to defective workmanship is unknown. A report of tests upon these two alloys, made at the Bureau of Standards, is cited for reference.¹

"Auranium" and "platino" are trade names for alloys of gold and platinum intended for use in the form of crucibles and dishes. Nothing is known as to their serviceability.

Several papers have been issued from the Bureau of Standards² that deal with the quality, behavior, and testing of ordinary platinum ware.

¹ Gurevich, L. J., and Wichers, E., *Jour. Ind. Eng. Chemistry*, vol. 11, 1919, p. 570.

² Burgess, G. K., and Sale, P. D., *Jour. Ind. Eng. Chemistry*, vol. 6, 1914, p. 452, vol. 7, 1915, p. 561; *Sci. Paper Bur. Standards* No. 254, 1915. Burgess, G. K., and Waltenberg, R. G., *Sci. Paper Bur. Standards* No. 280, 1916.

C. REAGENTS.

All analyses performed in the Survey laboratory have been made with the purest reagents obtainable, either by purchase in the open market or by special preparation on the part of manufacturers or in the laboratory, but the most ceaseless vigilance has at all times to be practiced. As is now generally known, a "C. P." or "analyzed reagent" label is no guaranty whatever of the purity of a reagent. Every new purchase must be examined if it is one in which purity is a desideratum. In general, all so-called "C. P." chemicals should at least stand the tests laid down by Krauch.¹ The "guaranteed" or special reagents, sold at high prices, have been found at times to be worse than those emanating from sources which make no claim to special purity for their goods.

Acids made in this country can be had of a high grade, and most of these need no redistillation except for special experiments, but exceptions have been noted.

Hydrofluoric acid had to be always freshly distilled with potassium permanganate until the introduction of ceresin bottles afforded an article sufficiently pure for the most exacting work. Care must be taken to see that no particles of paraffin or ceresin are floating on the acid as it is poured out, and that this is free from traces of hydrochloric acid whenever it is to be used for attacking silicates with a view to determining chlorine (24. C. b, p. 221). An important use for hydrofluoric acid is the decomposition of refractory silicates in the determination of ferrous iron. For this purpose it is necessary that it be free from any substance that will reduce permanganate. Sulphurous acid was found in one or two shipments, but this is a contamination against which care in manufacture can easily guard. On evaporation the acid should leave a nonvolatile residue so small as to be entirely negligible.

Ammonia water always ought to be redistilled at short intervals, after first shaking up with slaked lime in order to decompose any ammonium carbonate that it may hold. Glass stock bottles may be coated inside with ceresin so as to prevent contact between the glass and the ammoniacal solution, a device that may be serviceable with other reagents. For special purposes a small bottle of platinum or the cheaper gold can be used. Some manufacturers deliver in steel cylinders a very pure liquid ammonia, the use of which is to be preferred to that of commercial aqua ammoniae. A solution of any desired strength can be prepared as often as called for by collecting the gas from a cylinder in a bottle half full of water kept immersed in a bath of flowing cold water.

¹ Die Prüfung der chemischen Reagentien, 3d ed., Berlin, Julius Springer, 1896. English translation by J. A. Williamson, D. Van Nostrand Co., 1902.

Potassium bisulphate should be entirely free from silica, alumina, and heavy metals. The only correct way to get an accurate silica determination is to fuse the salt with a considerable amount of strong sulphuric acid, allow to cool, dissolve in water, and digest on the steam bath to coagulate the silica, which is then filtered; or the salt may be dissolved in water and evaporated with a large excess of sulphuric acid till fumes of the acid rise copiously. On cooling, the mass is dissolved and treated as above. If a satisfactory article is not to be purchased, it can be made from equivalent parts of potassium sulphate and sulphuric acid. Even then the normal salt must first be examined, for it has been found to contain notable amounts of lead, calcium, and silica. Sodium bisulphate is for some purposes preferable to the potassium salt. Both, however, should be converted to pyrosulphate by fusing in a large platinum dish and maintaining in fusion till all spattering has ceased and sulphuric acid rises copiously. The salt thus treated will not show the disagreeable frothing and spattering that is so objectionable when making fusions with the bisulphate, and it is more quickly effective.

The phosphorus ("microcosmic") salt used for precipitating magnesium has been found to contain iron and silicon.

Ammonium oxalate almost always contains calcium and must therefore be purified or specially prepared. The same may be said of oxalic acid. According to A. Classen,¹ ammonium oxalate sometimes contains lead.

Ammonium chloride has been known to contain manganese.

Hydrogen peroxide sometimes contains fluorine, which renders it unfit for use as a chemical reagent. The test for fluorine is carried out as follows: To 50 cm.³ of the reagent add a slight excess of sodium carbonate and warm the solution. Filter if a precipitate forms, and to the boiling solution add calcium chloride in excess. Filter and ignite the precipitate gently. Treat it with dilute acetic acid, drop by drop, till the calcium carbonate is dissolved, filter, wash, ignite the residue gently, and test it with strong sulphuric acid in the usual way for fluorine. The perhydrol of E. Merck, now unobtainable in this country, is a very pure and strong peroxide (30 per cent).

Sodium carbonate, one of the most important reagents in silicate analysis, sometimes can be had which does not carry more than 2½ mg. of total impurity (see 6. A. d. β, p. 94) in 20 grams (0.012 per cent). This should be reserved for the main portions, in which silica, alumina, etc., are to be determined. For other constituents, as phosphoric acid, fluorine, sulphur, a poorer grade is quite allowable, provided it is free from the element to be determined and from

¹ Zeitschr. anal. Chemie, vol. 42, 1903, p. 518.

any other which might interfere with its determination. Silica is to be tested for by evaporating the solution of the carbonate or the dry salt with sulphuric acid in large excess till fumes of the acid are copiously evolved, dissolving the cooled mass in water, and digesting on the steam bath in order to coagulate the silica before filtering. Evaporation with hydrochloric acid will not yield all of the silica. Once a very objectionable impurity in the otherwise acceptable article was encountered, namely, fluorine. The explanation of its presence is probably that cryolite had been used as the source of the carbonate. Sodium phosphate in small amounts seems to be a common contaminant of even good grades of sodium carbonate.

Sodium hydroxide made from sodium has been found with a large amount of lead, a fatal obstacle to successful mineral analysis, and also with small amounts of nickel.

Owing to the solvent action on glass of many solutions of solid reagents, these solutions should be made up at frequent intervals in small quantities, or, preferably, the solid should be dissolved as wanted. That this is no unnecessary refinement in really good work has been amply demonstrated, and it is particularly called for with such reagents as ammonium oxalate and microcosmic salt.

The quality of the distilled water used in analysis should be looked after particularly. The water should be tested at frequent intervals by evaporating at least a liter of it in a platinum dish with special precautions to exclude dust and chemical fumes. The best once-distilled water, evaporated under proper conditions, is likely to show a residue unignited of about 1 mg. After gentle ignition and removal thus of volatile salts the weight may be reduced to about 0.5 mg.

II.—METHODS APPLICABLE TO SILICATE ROCKS.

1. INTRODUCTORY REMARKS.

The order hereinafter followed in describing the various chemical separations has little relation to the affinities of the constituents of the rock, but those are grouped together which can be determined conveniently in the same portion of rock powder. Thus, in the main portion it is usual to determine SiO_2 , TiO_2 , MnO , NiO , CaO , SrO , MgO , total iron, and the combined weight of all the following: Al_2O_3 , TiO_2 , P_2O_5 , ZrO_2 , all iron as Fe_2O_3 , and nearly if not quite all vanadium as V_2O_5 , also perhaps rare earths if present. In a separate portion is estimated FeO , and also the total iron, as well as BaO , if these last are desired as checks. The alkalis need a portion for themselves. In another it is convenient to determine ZrO_2 , BaO , rare earths, and total sulphur. For V_2O_5 and Cr_2O_3 still another and usually much larger portion is to be used. Determinations of CO_2 , C , H_2O , F , and Cl are all made best in separate portions of substance, though various combinations are possible, as CO_2 and H_2O , C and H_2O , or H_2O , F , and Cl . In fact, by a judicious selection and combination of methods a very satisfactory analysis can sometimes be made on 4 grams of material without omission of anything of importance, though the time consumed will be greater than if ample material is available.

As an illustration of the advantage to be gained by a little judgment in the combination of methods, the case of sulphur, barium, zirconium, and rare earths may serve. Many chemists never look for any but the first of these, but by following the procedure given under 15. A (p. 170), not much more labor is expended in confirming their presence or absence than that of sulphur alone.

With only occasional exceptions nearly all the constituents mentioned on page 25 can be determined, if present, in portions of powder not exceeding 1 gram each in weight.

This is a convenient weight to take for the main portion, in which silica, alumina, etc., the alkaline earths, and magnesia are to be sought; but it should, in general, be a maximum, because if a larger quantity is taken the precipitate of alumina, etc., is apt to be unwieldy. It can not often be much reduced with safety if satisfactory determinations of manganese, nickel, and strontium are to be expected. For the alkali portion one-half gram is a very convenient weight. In general, it may be made a rule not to use more than 2

grams for any portion which has to be fused with an alkali carbonate, as for sulphur, fluorine, and chlorine. For carbon dioxide the weight may rise to 5 grams, or even more, if the amount of this constituent is very small, without expenditure of any more time than is required by 1 gram and with correspondingly greater approach to correctness in the result. For vanadium also usually a larger weight than 2 grams is demanded.

For the attainment of accurate results, such as are needed for the close classification of a rock in the system devised by Cross, Iddings, Pirsson, and Washington,¹ too great stress can not be laid on the exercise of the utmost care throughout the analysis. This applies not only to routine manipulations, but even more in the matter of double precipitations, where these are called for, and in the testing of filtrates and precipitates to insure complete recovery of the desired substances, on the one hand, and freedom of them when obtained from matter which should not be there, on the other. These cautions are especially applicable to analysts who have little experience. It must always be remembered that analysis can at best afford but approximate results, which will be more serviceable the greater the care bestowed in obtaining them.

2. SPECIFIC GRAVITY (POROSITY).

GENERAL REMARKS.

Though a knowledge of the specific gravity of rocks is seemingly less prized now than formerly by petrographers, it is occasionally needed and is ever a most important criterion in the identification of mineral species. As ordinarily obtained, whether by the method of suspension or by the pycnometer, the results fall short of the accuracy which is generally credited to them. A really accurate determination of the specific gravity of solids by the pycnometer, in which the error shall not exceed one or two points in the third decimal, is to be achieved only with the most painstaking precautions. (See 2. B. pp. 55-56.) Without this care the error in the second decimal may and often does amount to several points.² For these reasons the subject of specific gravity is treated in some fullness. Although the porosity of a rock is a constant seldom used by the petrographer, it is one that is most useful in the compara-

¹ Quantitative classification of igneous rocks, 286 pp., Univ. Chicago Press, 1903.

² H. LeChatelier and F. Bogitch (Compt. Rend., vol. 163, 1916, p. 459) claim that the influence of the adhering film of air gives rise to low results when specific gravities are determined in water and that accurate results may be obtained by the use of carbon tetrachloride, benzene (crystallized), or petroleum ether (essence minérale). They measure the volume displaced in a simple form of apparatus. However, they employed only reduced pressure and not boiling to remove the air film when using water.

tive study of building stones, and since its determination as often carried out is likewise faulty and gives a value which does not represent the pore space in terms of the volume of stone, it has been deemed expedient to devote space to this subject also, especially as the determination of porosity involves that of specific gravity.

A. BY SUSPENSION IN WATER.

a. ORDINARY METHOD FOR SPECIFIC GRAVITY.

The determination of specific gravity by suspension in water is best made on one or several fragments weighing up to 20 grams. They are held together by a fine platinum wire ready for suspension from the balance, and thus held are placed in a small beaker to soak over night in distilled water under the exhausted receiver of an air pump side by side with a similar beaker of water. Boiling, while effective as a means of removing air, should not be resorted to, because the boiling water may exert an undesirable solvent and abrading effect. In the morning the wire is attached to the balance arm, the rock fragments remaining immersed in the water; a thermometer is placed in the companion beaker of water, now likewise in the balance case, and the weighing and temperature reading are made at once. Both vessels of water having precisely the same temperature, it is quite unnecessary to wait for the water to assume that of the balance should it not already possess it. The fragments are now lifted out, without touching the vessel, and transferred carefully to a tared crucible or dish. The wire is removed and at once reweighed, with the precaution that it dips just as far into the water now as when weighed. Hereby a special weighing of the wire out of water is avoided. The sample may now be dried on the water bath and then at 110° for some hours to expel with certainty all absorbed water, and weighed after prolonged cooling in the desiccator. It is better to ascertain the weight of the dry rock after soaking in water than before, in order to avoid the error due to possible breaking off of a few grains between the two weighings. Should the density of the rock in air-dry condition be required, it may be left exposed to the air for a long period after drying and before weighing;¹ but the difference will affect the second decimal by more than a single

¹ In view of the uncertainty as to what constitutes hygroscopic water (see p. 72), this course is perhaps more to be commended than the former, and seems imperative for certain zeolitic rocks. In such cases it is best to weigh the fragments before putting to soak, and afterward to collect on a Gooch crucible the grains which may have fallen off in the water. Should no crucible of this kind be available, a paper filter may be used unhesitatingly and incinerated with the powder. Owing to the small amount of powder the error due to loss of even all its water during ignition is quite negligible.

Since the first publication of the foregoing in Bulletin 148, a series of determinations on eight rocks, in which the weighing was done after drying, led to an interesting observation. The lumps were heated for a short time on the steam bath until dry on the surface, then allowed to cool in air and weighed from time to time during two or three days. It

unit only in exceptional cases. For instance, an undried rock of 2.775 specific gravity containing in the uncrushed state the high percentage of 0.3 hygroscopic moisture will have a density of 2.79 when dry; a rock of 2.982 specific gravity, undried, will have a density of 3 after removal of 0.3 per cent of moisture. The difference becomes greater as the density of the rock increases.

This method of ascertaining the specific gravity of rocks is certainly more convenient than, and for compact rocks is believed to be decidedly preferable to, that of the pycnometer, in which the fragments must be reduced to small size with consequent formation of more or less powder, which is subject to slight loss in the various manipulations. To exclude this powder and employ only small fragments would introduce a possible source of error, for the powder is likely to consist largely of the most easily abraded minerals and consequently the fragments might not have the average composition of the mass. By following the instructions given above, loss of material is avoided absolutely, a decided saving in time is effected, and considerable weights can be employed with consequent lower probable error in the results. To vesicular rocks, however, notably certain lavas, the above procedure is of course inapplicable, as it is probable that many of the interior pores would be inaccessible to penetrating water.

D. METHOD FOR SPECIFIC GRAVITY AND POROSITY COMBINED.

E. R. Buckley¹ has called deserved attention to the faultiness of the methods generally employed for the determination of specific gravity and porosity as applied to building stones, and has brought together the fruits of his experience. His recommendations are essentially as follows:

The specimens should be cubes, such as are commonly employed for the other physical tests, measuring usually 2 inches square.

was observed that some lumps lost weight from the start, while others gained. For instance:

14. 3803	9. 5342	17. 0846
. 3730	. 5178	. 1089
. 3666	. 5121	. 1159
. 3483	. 5024	. 1413
. 3481	. 5016	. 1388
. 3450	. 5016	. 1370
. 3457		

The losses in the first and second cases may reasonably be ascribed to the gradual evaporation of water absorbed in the pores, while the increase in the third case is doubtless indicative of the presence of zeolitic constituents, from which even brief exposure to the heat of the steam bath had sufficed to drive out a good deal of their loosely held water. Subsequent careful analysis confirmed this view, for each rock that gained in weight was found to hold a relatively large amount of water removable at 105°, and the microscope revealed the presence of zeolitization in them and not in the others. Hence, this procedure may sometimes be of value as a test for the presence of zeolitic minerals in advance of or as confirmation of the microscopic diagnosis.

¹ Building and ornamental stones of Wisconsin: Bull. Wisconsin Geol. Nat. Hist. Survey No. 4, 1898, pp. 63, 70.



These are dried for at least 24 hours at 110° (100° is not high enough to insure the removal of all interstitial water) and weighed to centigrams. They are then placed on the bottom of a large bottle, the cork of which can be hermetically sealed. Through the cork pass three tubes, two of which end below the cork and connect with a vacuum pump and manometer, respectively. The third tube, provided with a stopcock, ends near the bottom of the bottle and leads on the outside into a basin of water which can be heated to boiling. The bottle itself rests in a water bath, so that its contents can be kept hot all the time. At first the cubes rest in a shallow layer of water only, the better to facilitate the escape of air and entrance of water under reduced pressure, which should not exceed one-twelfth of an atmosphere. The cubes should remain in this state for 72 hours, experiment having shown that little or no absorption takes place after this lapse of time. Water is let in slowly from time to time, till the cubes are wholly immersed. In this way, it is thought thorough saturation can be attained. The saturated samples are transferred to an open dish filled with water and taken to the balance, where their weight in water is ascertained by suspension. They are then removed from the water, rapidly dried on the surface with bibulous paper, and the weights then taken in air.¹ They are dried at 110° for 24 hours and again weighed. The second dry weight was found by Buckley to vary from the first rarely by as much as 0.2 gram, and often by not more than 0.01. "When reckoned in per cent, the error would be such a small fraction of 1 per cent as not to be worthy of attention. The specific gravity was determined by dividing the average of the two dry weights by the difference between the dry weight and the weight of the cube suspended in water." For arriving at the true porosity or actual pore space compared with the volume of the sample tested, the following formula is to be used:

$$\frac{(B-A) \text{ sp. gr. } 100}{(B-A) \text{ sp. gr.} + A} = P$$

in which A is the average dry weight, B the saturated weight, and P the percentage of porosity or actual pore space. The value thus

¹ The above procedure differs from that of Buckley in the inversion of the order of weighing in water and after wiping. The more perfect the vacuum the less need be the temperature of the bath of immersion to insure the effective aid, by boiling of the water drawn up into the pores of the specimen, in securing expulsion of the inclosed air. A vacuum desiccator can perhaps be substituted for the bottle with much advantage. It will not be necessary to open the desiccator for the periodic introduction of water if to the evacuating tube is attached a Y or T with stopcocks, one branch leading to the pump and manometer, the other to a basin of water. By proper regulation of the cocks water can be drawn in at pleasure. In a later publication (Missouri Bureau Geol. and Mines, 2d ser., vol. 2, 1904) Buckley states that he has reduced the time of immersion to 24 hours and the vacuum to one-fourth of an atmosphere without finding appreciable differences in the results obtained.

obtained is always much higher than that ordinarily taken as the measure of porosity. This last would better be called, according to Buckley, "ratio of absorption," being found by dividing the weight of water absorbed by the dry weight of the stone and multiplying by 100. Buckley finds no definite relation between porosity and ratio of absorption, although in a general way the former is a little more than twice the latter.

In calculating the weight of a stone in pounds per cubic foot the pores should be included in this volume. The weight sought is found by multiplying the apparent specific gravity by 62.5—that is, by the weight of a cubic foot of water. The apparent specific gravity can be calculated from the above data by the formula

$$\frac{A}{B-C}$$

in which A is the dry weight, B the saturated weight, and C the weight in water.

T. W. Thörner¹ and H. Seger and E. Cramer² have described apparatus alike in principle for determining porosity by the use of which a direct specific-gravity determination is avoided and the operations are very simple. The apparatus of Seger and Cramer are of simpler construction than those of Thörner, and have stood the test of many years' use. By both, however, the true porosity as well as the "ratio of absorption" is ascertainable.

In the Proceedings of the American Society for Testing Materials for 1918, page 588, is given a tentative standard method for the determination of porosity and volume changes in refractory materials.

C. PENFIELD'S METHOD FOR MINERAL FRAGMENTS.

Penfield³ recommends the following modification of the suspension method as more convenient than that by the pycnometer in many cases for small fragments of minerals.

After boiling in water, the substance is transferred with water to a small glass tube about 8 by 35 mm., provided with a fine platinum wire for suspension. This is weighed full of water in another vessel of water, and again after the removal of the mineral, the weight of which is found after drying.

The method is of course more applicable to homogeneous minerals than to rock fragments and will therefore be applied in rock analysis chiefly to the determination of the specific gravity of the mineral grains separated by heavy solutions or acids.

¹ Chem. Zeitung, vol. 29, 1905, p. 744.

² Idem, p. 884.

³ Am. Jour. Sci., 3d ser., vol. 50, 1895, p. 448.

B. PYCNOMETER METHOD.

a. ORDINARY METHOD.

For determining the specific gravity of materials of fine grain the pycnometer method has to be used. A good procedure is that adopted in the Survey laboratory by L. G. Eakins a number of years ago, provided there is no evaporation whatsoever around the stopper of the pycnometer, a condition seldom, if ever, fulfilled, unless a thin film of vaseline is used, the weight of which need not exceed half a milligram. The pycnometer used is one with a capillary stopper, provided with a millimeter scale etched in the glass, the divisions being numbered both ways from the center and calibrated by mercury, so that the value of each one in weight of water is known. The capacity of the flask filled with water to the zero division is then calculated for every half degree of temperature from 0° to 30° by making a series of careful weighings in which, the capacity of the stem being known, it is quite immaterial at what level the water stands, provided it is within the limits of the scale. The exact temperature is obtained by an accurate thermometer placed in a companion vessel of shape similar to that of the pycnometer and containing a like amount of water, both being left in the balance case till its temperature has been nearly or quite assumed, as shown by a second thermometer. The weighing must of course be made before the thread of water has sunk beneath the lowest division, which it will do after a time, even though at first filling the bore to the top of the stopper; and the corrected weight of the flask full of water to the zero mark is found by adding or subtracting the needed amount, as shown by the height of the thread on the scale.

For each of the pycnometers in use, and they are of different sizes, is prepared a table showing its weight, the value of each scale division in grams of water, and the capacity of the flask at different temperatures, as indicated above. The preparation of such a series of flasks is time saved in the end, for the weighing of the flask full of water each time a density determination is made is rendered superfluous. All that is necessary is to look up in the table the weight corresponding to the temperature.

The density of the previously weighed substance is now determined in much the same way as in A. a, page 50, after the unstoppered pycnometer containing it and nearly filled with water has stood with its companion vessel of water under the air pump the necessary length of time. The water needed to fill the flask is taken from its companion.

All who have used the pycnometer method for fine substances know the difficulty experienced in preventing some of the material from

being held at the surface, despite all attempts at making it sink. Hence it often happens that a very small portion runs out around the sides of the stopper on inserting it. If the flask rests in a small tared dish the grains thus forced out may be washed down into it and weighed after evaporation in order to get the correct weight of what is in the flask; or, after weighing, the contents of the flask may be emptied into a tared dish and the water slowly evaporated off in order to get the weight of the mineral. Usually this way is less to be recommended than the other.

b. REFINED METHOD.

In their elaborate study of the thermal properties of the feldspars¹ A. L. Day and E. T. Allen found the ordinary methods of specific-gravity determination of powders by the pycnometer to be affected with grave errors. To eliminate these in great degree they use special pycnometers and precautions (slightly modified since publication) which are described in the paragraphs that follow. With 25-cm.³ pycnometers and 5 to 10 grams of material of from 2.50 to 2.75 specific gravity the error from all causes should never be greater than one unit (± 1) in the third decimal place.

A chief source of error is the evaporation of water around the stopper. In order to reduce this to a negligible quantity, the grinding should be very fine and the stopper should be vaselined slightly before the final weighing. If the excess of vaseline is carefully wiped off, the error due to its weight will not affect the result in the third decimal with 25-cm.³ flasks. The best flasks are those with capillary stoppers, made with the glass of the necks 2 mm. thick, so as to avoid springing when the stopper is pressed in, and ground square off to prevent the adhesion of a film of water between stopper and neck above the joint. With the stopper slightly vaselined, such a flask does not lose at 30° more than 1 to 1½ milligrams of water per half hour.²

To obviate another serious source of error,³ incomplete removal of air from the powder and undue loss of powder during filling and stoppering, the device of G. E. Moore⁴ is used, slightly modified, as shown in figure 8. The flask containing the powder is attached to a

¹ Pub. Carnegie Inst. Washington No. 31; and in less detail in *Am. Jour. Sci.*, 4th ser., vol. 19, 1905, p. 93; *Zeitschr. phys. Chemie*, vol. 54, 1905, p. 1.

² J. Johnston and L. H. Adams (*Jour. Am. Chem. Soc.*, vol. 34, 1912, p. 567) have modified the pycnometer with the object in view of attaining still greater accuracy. The new feature is a plane ground joint between bottle and stopper. The neck of the bottle is made especially thick at the upper end in order to provide sufficient surface for the cap to rest upon. The cap is not perforated, but its lower face and the top of the neck are made optically flat so as to give a perfect joint that allows no escape of water. Such perfect surfaces are very difficult to prepare. With this instrument the results differ only in the fourth decimal, a degree of accuracy quite uncalled for with rock powders.

³ See footnote 2, p. 49.

⁴ *Am. Jour. Sci.*, 3d ser., vol. 3, 1872, p. 41; *Jour. prakt. Chemie*, vol. 2, 1870, p. 329.

water pump, with the intervention of a tube and bulb attachment, as shown. The bulb A contains boiled water. When the system has been nearly freed from air by the pump, water from A is made to flow into the flask. Then by tapping and plunging the flask into water warmed to 40° to 50° , in order to produce boiling within the flask, the air is soon removed. During the boiling powder will usually be thrown up into the connecting tube; but this can be washed back by water from A or, after disconnecting, by boiled water from a wash bottle. Should any particles remain in the tube, they are washed into a tared dish and weighed, after evaporation of the water. It is absolutely essential that not the smallest grain be caught between the stopper and the neck. To this end the neck is wiped out with a bit of filter paper, which is burned in the tared dish in order to obtain the proper correction.

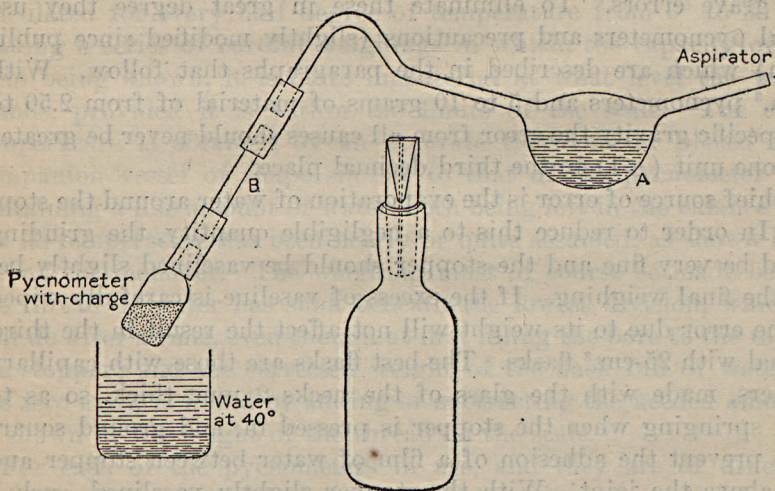


FIGURE 8.—Moore's device to remove air from mineral powders.

Constant temperature is attained in a water thermostat electrically regulated to tenths of a degree at a temperature slightly above that of the balance case. In the thermostat there is also placed a small vessel with water for the final filling. If the powder is very fine, the flask may have to remain in the thermostat several hours to allow complete settling before wiping the neck, vaselining, and stoppering. When the flask is filled and stoppered, it should be returned to the thermostat for a time, with a short piece of rubber tube slipped part way over the end of the stopper, so as to form a cup for a drop of water and insure that the capillary remains filled. At the proper time the rubber is removed and the flask wiped quickly with bibulous paper and weighed without delay. A blank test must of course be made with water alone, or the pycnometer may be calibrated once for all within any desired range of temperature. A determination of

the accuracy attainable in this way is subject to a correction for buoyancy.

(See p. 70 for remarks by Day and Allen on another source of error in the determination of the specific gravity of powders.)

C. HEAVY SOLUTIONS NOT SUITABLE FOR ROCKS.

Because of their roughness, porosity, and complex mineral composition the density of rock fragments can not be determined accurately by that of heavy solutions in which they may remain suspended.

3. PREPARATION OF SAMPLE FOR ANALYSIS.

A. QUANTITY OF ROCK TO BE CRUSHED.

The amount of material that must be used in preparing the analysis sample varies. Most rocks are well represented by a few chips from a hand specimen, but if a rock in which porphyritic structure is strongly developed is to be analyzed a large sample should be provided, gaged according to the size of the crystals, and the whole of this should be crushed and quartered down for the final sample. Unless this is done, it is manifest that the analysis may represent anything but the true average composition of the rock. The geologist should see that a fairly representative sample is provided, else the chemist's work, however careful, may count for little.

B. CRUSHING.

For accurate analyses the use of steel power crushers and mortars is out of the question because of the danger of contamination by particles of metal and the impossibility of cleansing the roughened surfaces after they have been in use a short time. Extraction, by the aid of a magnet, of steel particles thus introduced into the powder is quite inadmissible, for the rocks themselves, almost without exception, contain magnetic minerals.

a. SURVEY METHODS.

For breaking large pieces of rock to small sizes a thick steel plate with specially hardened surface and a similarly hardened pounder, such as street pavers use, will probably render the best service, but the hardening must be done with extreme care.

A method of rough crushing on a small scale that gives fair satisfaction in practice is to place each fragment as received on a hard steel plate about $4\frac{1}{2}$ cm. thick and 10 cm. square, on which is likewise placed a steel ring 2 cm. high and of about 6 cm. inner diameter, to prevent undue flying of fragments when broken by a hardened ham-

mer. In this way a considerable sample can soon be sufficiently reduced for transfer to the agate grinding mortar with a minimum of metallic contamination.

This method is now superseded in the Survey laboratory by one devised by C. W. H. Ellis, mechanician in the geophysical laboratory of the Carnegie Institution, which entirely obviates loss of material by flying fragments. The method of operating is apparent from

figure 9. The block, cylinder, and pestle are of the best chilled tool steel, surface hardened to the utmost limit. The cylinder fits snugly into a depression in the block, after the manner of an ordinary "diamond" mortar, but the pestle has a diameter less than the inner diameter of the cylinder. The crushing is done by the pestle, without the aid of a hammer, and may be carried so far, if necessary (see C, p. 60), as to furnish by the aid of a fine sieve, preferably of the best silk bolting cloth, a powder that is fit for analysis without needing further pulverization in a mortar. For very many rocks and minerals a material that passes a sieve of 30 meshes to the linear centimeter can be used directly for the analysis. Much the greater part

FIGURE 9.—Ellis's mortar for crushing coarse materials. All parts of best chilled and surface-hardened tool steel. A, Block, $12\frac{1}{2}$ by $12\frac{1}{2}$ by 6 cm., with depression in center 0.6 cm. deep; B, pestle, 20 cm. high, 3.5 cm. diameter at base; C, cylinder, $12\frac{1}{2}$ cm. high, 5 cm. outside diameter, 4.4 cm. inside diameter, fitting accurately the depression in the block.

of this will consist of grains of a diameter less than that of the mesh of the sieve, even when the intervals between successive applications of the pestle and siftings are very short.

Metal sieves must on no account be used if search is to be made for elements identical with those of which the sieves are made.

An imperative precaution, when using either of these methods, however, is to refrain absolutely from the least grinding or rubbing motion, with the hammer in the one case or the pestle in the other. Even quartz can be broken down by vertical blows to a size fit for the agate mortar without showing any darkening in color, whereas if a rubbing motion has been employed to even a slight extent, the powder will, by contrast, be perceptibly dark after grinding in the

mortar. The hardest steel is very susceptible to abrasion by minerals less hard than quartz.¹ The crushing must be carried to such a degree of fineness that after transferring the grains to the mortar the grinding motion of its pestle will not occasion further loss of flying particles because the portions lost will not have the same composition as those retained unless the material is glassy or very fine-grained.

If grinding is not to follow crushing, the sieve should be chosen of a mesh that will afford a powder susceptible of complete or nearly complete decomposition within 20 minutes by boiling with dilute hydrofluoric acid (see C, below, and 21. A, p. 192). In order to obtain the minimum of "flour" it is important to sift at very frequent intervals. Some flour is, however, essential to the production of a homogeneous sample when flaky minerals, like the micas, are present. If the flour is first separated from a micaceous powder, no amount of mixing of the coarser material will afford a sample in which the mica does not show in streaks instead of being uniformly distributed. The sample finally obtained is to be very thoroughly mixed on glazed paper or by gentle shaking in a clean bottle.

D. WASHINGTON'S METHOD.

The rock is first reduced, as by the methods described in a, to lumps that will fit into a "diamond" steel mortar of Plattner's form, the bottom of the cavity being hemispherical and matched in shape by the end of the pestle. The lumps are crushed, one by one, in the mortar by a dozen blows of a half-pound hammer (billet of wood, Dittrich), and the contents of the mortar are emptied into a cylindrical glass box about 3.5 cm. deep and 7.5 cm. in internal diameter, with walls about 2 mm. thick. When the whole sample, or a quartered portion if large, has been thus crushed a piece of best silk bolting cloth with about 25 meshes to the linear centimeter is stretched over the open side of the box and clamped fast by a brass ring 1 cm. in height. The box is now inverted and the finest powder gently sifted onto a sheet of glazed paper. The material left on the cloth is recrushed in the mortar and resifted, these operations being repeated until nearly all has passed the sieve. The final small oversize portion is ground in an agate mortar. It will, of course, not do to

¹ When the crushing has been done with proper care, the amount of steel contaminating the sample is so small as to cause no important error. This steel is for the most part apparently not in splinters but as thin films on the mineral grains. Its presence can be shown readily by grinding the crushed sample to a very fine powder in presence of water. The films thus become separated from the grains and still further flattened, and as the grinding progresses they rise as a visible scum to the surface of the water, whence they can be removed by careful handling of a magnet. This behavior of the films might perhaps afford a means of testing for native iron in rocks, provided the use of steel for crushing could be avoided altogether.

reject any portion, for thereby the composition of the mass will be affected.

Washington finds that in this way there is no danger of serious contamination by metallic iron (see preceding footnote) and that any error resulting from the introduction of cloth fiber is negligible. This last will hardly be true of the method practiced in parts of Europe (the German "beuteln"), which, at least as it was carried out in Bunsen's laboratory, differs in essential points from the gentle sifting recommended by Washington.

C. GRINDING.

Ordinarily an extremely fine state of division of the analysis sample is unnecessary, except for those portions in which alkalis and ferrous iron are to be determined or where soluble constituents are to be removed by acids, etc., and for such portions the final grinding can be done at the balance table on a small quantity of the crushed sample.

Not only is fine grinding for most purposes needless, but it may be positively harmful, allowing escape of contained gases, and, as R. Mauzelius has shown,¹ it is absolutely imperative for the correct determination of ferrous iron to use the coarsest powder that can be decomposed completely by the method of attack employed. I have since shown² that this is true for the water that is not given off at 100°-110°. Mauzelius finds that the finer the material (containing ferrous iron) is ground the less ferrous iron is found. In all his experiments on rocks and on iron-bearing minerals separated from rocks the oxidation was marked and in the most extreme case amounted to about 40 per cent of the total ferrous iron (3.13 per cent FeO found in the finest powder against 5.13 per cent in the coarsest). This totally unexpected behavior has been confirmed by me. (See 21. A, p. 189.) The necessity for an entire reversal of the hitherto prevalent practice of preparing a very fine powder for the ferrous-iron determination is obvious.

The preparation of two samples, one coarse for the ferrous iron and another much finer for the other constituents, though perhaps unavoidable at times, is objectionable for several reasons. (1) The finer the powder the more loosely held (hygroscopic) water it contains, easily 5 to 20 times as much as unground grains, and also the

¹ The determination of ferrous iron in rock analysis: Sveriges geol. Undersökning, Arsbok 1, 1907, No. 3.

² The influence of fine grinding on the water and ferrous iron content of minerals and rocks: Jour. Am. Chem. Soc., vol. 30, 1908, p. 1120; Chem. News, vol. 98, 1908, pp. 205, 215. J. W. Mallet (Phil. Trans., vol. 171, 1880, p. 1017) seems to have been the first to notice that mechanical crushing could expel water from hydrous minerals (alum). He ascribed the effect to heat developed by the crushing, a view with which I am in accord. Carey Lea (Phil. Mag., vol. 34, 1892, p. 36; vol. 37, 1894, p. 31), however, regards mechanical stress, especially shearing stress, as the effective factor.

more water that is not given off at 100°. If two samples are used the water given off both below and above 100° must be determined in each and a correction applied to the other constituent or constituents that may be determined in the finely ground sample. (2) The composition of the unground sample will differ in another respect from that of the ground material by the amount of silica derived from the mortar. This may easily reach or exceed one-half of 1 per cent of the weight of the mineral powder (see p. 63), depending on the hardness of the minerals and on the length of grinding.

In order to obviate the need for two samples I have made experiments with a view to secure fine grinding and at the same time avoid oxidation. These experiments need to be multiplied before positive conclusions can be reached and precise directions formulated. So far as they go, however, they show that grinding in a nonoxidizing medium, such as absolute alcohol, is fairly satisfactory. Water is somewhat less satisfactory, notwithstanding the lower solubility in it of oxygen.¹ Alcohol does not seem to exercise a reducing effect on ferric minerals when they are ground in it. These experiments have served to show at the same time that the oxidation of the iron is not due merely to the greater exposure of surface, but that it is probably aided by intense local heat from friction and fracture of the grains under the pestle. Probably grinding in an inert gas would be more satisfactory, but while this might be arranged with a mechanical grinder, it would be impossible when the grinding has to be done by hand, and in any case it would involve much inconvenience and trouble. When alcohol is used, it should be in small quantities at a time, enough to wet the powder thoroughly and to give a very liquid mass. A second and third application of alcohol are sometimes needed, because of the rather rapid evaporation. When the grinding is finished the alcohol is allowed to evaporate spontaneously under a cover placed a few centimeters above the mortar and pestle, so as to exclude falling dust and yet allow free circulation of air. When thoroughly free from alcohol the powder is removed gently from mortar and pestle with a flexible knife blade and then bottled.

Formerly all rock samples in the Survey laboratory were, after crushing, reduced to powder by hand grinding, with expenditure of much time and labor. Since then, except in special cases, the work has been done by mechanical grinders run by a small electric motor. It will be evident from the foregoing statements, however, that hereafter such grinders are likely to be less used than they have been.

The grinder manufactured by the McKenna Brothers Brass Co. (Ltd.), Pittsburgh, Pa., is shown in figure 10, with the addition of simple attachments intended to keep metal dust and oil out of the

¹ Hillebrand, W. F., Jour. Am. Chem. Soc., vol. 30, 1908, p. 1120; Chem. News, vol. 98, 1908, pp. 205, 215.

mortar. These additions have been found to be quite essential for the Survey work. As made for the technical industries the machine is largely of brass, nickel plated, but the latest made for the Survey

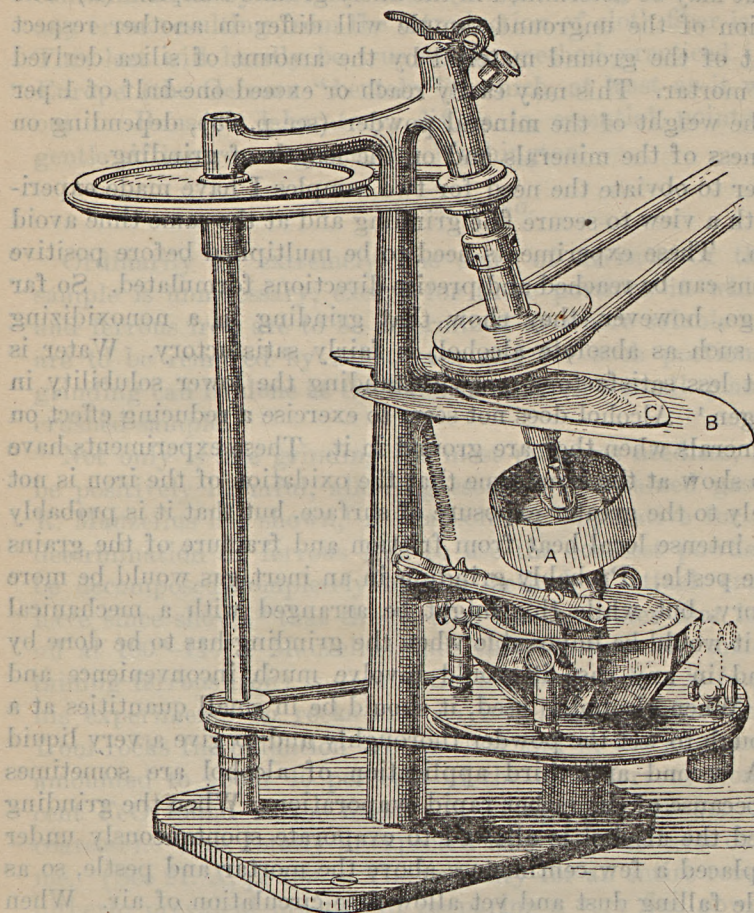


FIGURE 10.—McKenna ore grinder, slightly modified by the addition of the following attachments to prevent oil and dust from belts and bearings from entering the mortar. A, Copper cup soldered to head of pestle holder. This partakes, without the slightest friction, of the motion of the latter. B, Tin plate with deep sinus, the latter being covered in turn by the rubber cloth, C, which fits closely about the metal shaft. "The spring at the top of the sliding rod, to which the agate pestle is attached at the bottom, can be adjusted to give any desired pressure or can be thrown back entirely to allow the pestle to be raised in removing the agate mortar. This is accomplished by loosening a set screw and dropping one of the four posts holding the mortar in place. The pestle should make about 200 revolutions per minute, the mortar moving very slowly in the same direction. The scraper keeps the ore in the center of the mortar and the combined rolling and sliding motion controlled by the ball and socket supporting side arm reduces the hardest ore very rapidly."—Iron Age.

is of steel throughout, without plating. It was found that the pulley belts caused too much abrasion of the softer metal to permit its use for much of the Survey work, on account of the danger of copper,

zinc, and nickel getting into the sample in traces, and that in spite of a very limited use of oil this invariably became scattered over the contents of the mortar, though its presence never became visible to the eye except when white materials were ground. The last contamination is prevented by the copper cylinder, A, soldered securely onto the pestle holder so as to form a cup large enough for the purpose intended. The tin shield, B, with a superposed rubber cloth, C, covering the slit required for the proper adjustment of the shield, greatly lessens the danger of metallic contamination, even with the all-steel machine. At first it was thought that a rubber cloth covering the mortar, with the pestle snugly fitting a hole in the cloth, would be an effective protection, but it was found that there was sufficient friction on the rubber itself to cause contamination of the powder beneath.

With this apparatus a large amount of work can be done in a short space of time though there is much loss of fine powder if the speed of revolution is too high. In the Survey laboratory three of these machines are operated, one or all, on a single table from the same shaft, the whole being covered with a glass case divided by glass partitions, so as to exclude dust from the room and to separate the grinders.

D. ABRASION OF MORTAR AND PESTLE.

The abrasion of crushing apparatus has been touched on in B.

The abrasion of pestle and mortar becomes far more manifest with machines like that shown in figure 10 than with hand grinding, notwithstanding the fact that each has its motion simulating as far as possible that of the hands. There is undoubtedly a very considerable introduction of silica into the sample from these sources, but in comparison with the amount invariably present in an igneous rock the quantity abraded is hardly of moment. Rocks normally free from silica, or nearly so, like many iron ores, are as a rule softer than igneous rocks and consequently cause less abrasion of the grinding implements.

E. T. Allen, in order to get an idea of the amount of silica introduced into an ordinary rock sample through the abrasion of the grinding implements, caused 200 grams of quartz sand to be ground in portions at a time till all passed a sieve of 150 meshes to the linear inch (60 to the centimeter), the time required being 19.5 hours. The mortar (635 grams) lost 0.189 gram in weight and the pestle (268 grams) lost 0.102 gram, a total of 0.291 gram, or 0.145 per cent of the weight of the sand. The powder obtained in this case was less fine than that ordinarily sought at that time by rock analysts, but, on the other hand, the material was all quartz, a mineral much harder than most of those constituting the average rock.

W. Hempel¹ has tested experimentally the effect of grinding in mortars of agate, glass, iron, and hardened steel and has found that for hard bodies, like glass, hardened steel is far superior to agate, and that even mortars and pestles of green bottle glass showed much less abrasion than agate. In grinding 10 grams of glass to very fine powder the agate mortar and pestle, weighing 416 grams, lost 0.052 gram in weight (or 5 mg. per gram of glass), against a tenth of that loss with a hardened steel mortar and pestle of the same weight that had been some time in use.

Notwithstanding these observations in favor of steel, the use of metal in rock analysis is, as said above, forbidden by the conditions of the case. Still more so is that of glass because of its complex composition. If impurity can not be avoided, it is far better that it should be of one kind only, and that one productive of less disturbance than any other.

E. WEIGHT OF SAMPLE.

The sample when crushed or ground should weigh not less than 10 grams, and preferably 20 in case it should be necessary to repeat or advisable to employ unusually large portions for certain determinations, notably carbonic acid. Rock analysis has in this respect an advantage over mineral analysis, as rock material is almost always available in ample quantity and any desired number of separate portions may be used, whereas with a mineral the analyst is frequently compelled to determine many or all constituents in a single, perhaps very small portion of the powder. This course often involves delay and the employment of more complicated methods of separation than are usually necessary in rock analysis.

4. WATER—GENERAL CONSIDERATIONS.

A. THE RÔLE OF HYDROGEN IN MINERALS.²

As the purpose of this bulletin is primarily the instruction and guidance of the analyst, it has been thought best to curtail the discussion of the rôle of hydrogen in minerals given in the last edition, and to include here only such data as are likely to be of direct aid in the interpretation of the analytical results. Fuller discussions of certain more general aspects of the subject will be found in the

¹ Zeitschr. angew. Chemie, 1901, p. 843.

² This section was prepared by Edgar T. Wherry, H. E. Merwin, and Elliot Q. Adams, on the basis of the matter on this subject in Bulletin 422.

works listed in the footnote,¹ although it should be noted that the changes in viewpoint as to crystal structure, solid solution, etc., during recent years render many of the conclusions of the earlier writers of doubtful validity.

a. CONDITIONS IN WHICH HYDROGEN MAY OCCUR.

The table which follows presents a classification of the ways in which hydrogen (especially that given off as water) may occur in minerals, representing an enlargement upon the "provisional classification" given in Bulletin 422. In using this table it should be borne in mind that the subdivisions are not, in general, sharply delimited, but that a certain amount of gradation between them exists; that a given mineral may contain hydrogen in several different forms; and that some of the hydrogen originally present in one form may pass into another on grinding or on heating.

Classification of the condition of hydrogen in minerals, mineral aggregates, and mineral powders.

A. Essential hydrogen—present in regular atomic arrangement in molecular or crystal structure.

I. Present in definite, stoichiometric proportions.

- a. As hydrogen—called acidic by analogy to behavior in solutions.
- b. As hydroxyl—the hydrogen called basic, again by analogy.
- c. As water—especially water of crystallization.

II. Not present in stoichiometric proportions with reference to the substance as a whole, but present, in one of the above forms, in one or more of the constituents of mix crystals, including isomorphous mixtures.

B. Nonessential hydrogen—its presence not necessary for characterization of the mineral. (Considered as water or other compounds.)

I. In liquid solution, specially in deliquescent powders, also in amorphous material, including undercooled liquids.

II. Held by surface forces.

a. Absorbed on surfaces in films of molecular thickness.

1. On walls of cavities within grains of aggregates.
2. On exteriors of grains.

¹ Le Chatelier, H., *Zeitschr. physikal. Chemie*, vol. 1, 1887, p. 396; *Compt. Rend.*, vol. 104, 1887, pp. 1443, 1517; *Bull. Soc. franc. min.*, vol. 10, 1887, p. 204.

Hamberg, A., *Geol. Fören. Förh. Stockholm*, vol. 12, 1890, p. 591.

Tammann, G., *Zeitschr. physikal. Chemie*, vol. 10, 1892, p. 255; *idem*, vol. 27, 1898, p. 323; *Zeitschr. anorg. Chemie*, vol. 15, 1897, p. 319.

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Tschermak, G., *Zeitschr. physikal. Chemie*, vol. 53, 1905, p. 349; *Zeitschr. anorg. Chemie*, vol. 63, 1909, p. 169.

Panichi, U., *Pubbl. Inst. studi pract., etc., Sez. di sci. fis. e nat.*, 1908, p. 1. Lengthy abstract in *Neues Jahrb.*, 1910, Band 2, p. 2 of Referate.

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Thugutt, S. J., *Centralbl. Mineralogie*, 1909, p. 677.

Beutell, A., and Blaschke, K., *Centralbl. Mineralogie*, 1915, pp. 4, 195.

Langmuir, I., *Jour. Am. Chem. Soc.*, vol. 40, 1918, p. 1361.

B. Nonessential hydrogen, etc.—Continued.

II. Held by surface forces—Continued.

b. Held by capillarity, in liquid form.

1. In colloids with mesh structure.
2. In definite openings within grains of aggregates.
3. In spaces between separate grains.

III. Included.

- a. As liquid droplets in cavities.
- b. As included grains of minerals belonging to one of the above listed classes.

The following notes will help to interpret the table.

A. I. Investigations by X-rays and infra-red radiation indicate that groups, such as OH and H_2O , may have identity within crystals, so the separation of essential, stoichiometric, hydrogen into three classes, a, b, and c, is believed to be justified.¹

A. II. This class is intended to include such minerals as topaz, which is believed to consist of an isomorphous mixture of two end members, one hydrous and the other anhydrous, $Al_2(OH)_2SiO_4$ and $Al_2F_2SiO_4$. As the proportion of these members may vary widely, the hydrogen content may vary also; but even though the hydrogen is not present in stoichiometric proportions with reference to the mineral as a whole, it does bear definite relations to one of the constituent members and is therefore properly considered as essential. It is not necessary, however, that the members entering the substance be isomorphous in the strictest sense—that is, of homologous formula type; for instance, the mineral turgite is believed to be made up of two components Fe_2O_3 (hematite) and $FeO(OH)$ (goethite), in variable proportions, forming mix crystals.²

B. I. The liquid surrounding deliquescent crystals belongs here. A part of the water in opal may be dissolved, but probably most of it falls in B. II. b. 1, where the water of most hydrous "amorphous minerals" is thought to belong. Such substances as liquid hydrocarbons and volcanic glass, though not strictly minerals, may be mentioned here.

B. II. a. Adsorption of water in molecular films upon surfaces is believed to be a general property of solids, and if the surface exposed is large in proportion to the amount of material involved, the quantity of water thus held may be analytically significant. The increase in water content shown by many minerals upon fine grinding represents, thus, chiefly an increase in class B. II. a. 2. A few instances are known where water of class B. II. a. 1 is present in appreciable amount, one being the fibrous form of goethite, which is generally known as limonite.³

B. II. b. 1. With reference to this class it may be pointed out that recent studies of colloids, among which are to be included many "amorphous minerals," have shown that they often possess a submicroscopic mesh structure, water (or other liquid phase) being held in the interstices of this structure. It is possible that certain crystalline substances, and in particular certain of the zeolite minerals, may contain water in this form also, but this has not been convincingly demonstrated. Classes 2 and 3 under this heading are of special significance in connection with finely fibrous minerals, such as the above-mentioned goethite which often contain considerable amounts of capillary water.

¹ Coblenz, W. W., Pub. Carnegie Inst. Washington No. 65, 1906; Bull. Bur. Standards, vol. 2, 1906, p. 457. Schaefer, C., and Schubert, Martha, Ann. Physik, vol. 50, 1916, p. 339, Johnson, A., Physikal. Zeitschr., vol. 15, 1914, p. 712.

² Posnjak, E., and Merwin, H. E., Am. Jour. Sci., 4th ser., vol. 47, 1919, pp. 325, 337.

³ Idem, pp. 311-348.

B. III. Liquid inclusions of either water or hydrocarbons and solid inclusions of hydrous minerals may be the source of a considerable content of hydrogen.

D. BEARING OF THE CLASSIFICATION ON ANALYTICAL PROCEDURE.

α. Behavior of hydrogen on grinding the mineral.—The fine grinding of minerals may lead to either an increase or a decrease in total hydrogen content. (See B, p. 69.) An increase is the result of the subdivision of grains and the consequent development of a greater surface upon which water can be absorbed and otherwise held. A decrease is for the most part due to decomposition caused by local heating—by pressure or by mere change in grain size.

As in general (though by no means invariably) the decomposition temperatures of minerals containing water of crystallization are lower than those of minerals belonging to other classes, a marked loss of hydrogen on grinding may be regarded as pointing to the probable existence of the hydrogen in this form (A. I. c). Members of other classes, however, show low decomposition temperatures with sufficient frequency to render it unsafe to depend too much on this criterion. A decrease may of course also be due to the evaporation of water or other hydrogen-bearing liquids originally included as droplets (class B. III. a) when the grinding exposes them. It is to be inferred from the foregoing discussion that in order to be representative of the mineral the sample to be used for determination of water should be ground as little as possible; still the material must be fairly well subdivided in order that the water shall be liberated within reasonable limits of time and temperature. The effect of grinding on the water content may have at least confirmatory value in the final conclusion as to the rôle of hydrogen in the substance.

β. Behavior of hydrogen on desiccation at constant temperature.—On exposure of a mineral containing essential hydrogen which is given off as water to an atmosphere in which the partial pressure of water vapor is being continuously diminished, water is likely to be lost discontinuously. Hydrogen of class A. II may, however, behave differently; this class requires further investigation.

The behavior of nonessential hydrogen is likely to vary with the class concerned. If it is included (class B. III. a and b), no loss is to be expected. If it is held by capillarity (B. II. b), the mode of loss will depend on the size and shape of the capillary openings. Water absorbed on the surfaces of grains probably will be lost continuously—that is, it will be given off gradually as the water-vapor pressure diminishes, and dehydration will not be complete at any definite pressure. Hydrogen dissolved in “amorphous” material (B. I) would be expected to behave likewise.

The change here described is often reversible, water that has been lost by decreasing the aqueous vapor pressure being taken up again when this pressure is increased. Such rehydration may often be more readily followed than the original loss of water, and the continuity or discontinuity of the effect be more certainly determined thereby. In any thorough study of the rôle of hydrogen in a mineral, both dehydration and rehydration data should be obtained and preferably represented graphically, for conclusions as to the relations existing are often best drawn from the examination of curves.

γ. *Behavior of hydrogen (expelled as water) on heating.*¹—The behavior of hydrogen which is expelled as water on heating a mineral substance may be considered under three heads.

1. Heating to approximately constant weight at each step of a series of increasing temperatures in an atmosphere of uniform or regularly changing and usually small water-vapor pressure.

Minerals containing essential hydrogen are likely to lose it discontinuously—that is, at one or more rather definite temperatures. The temperatures at which dehydration occurs in dry air depend chiefly on the element or elements with which the hydrogen, hydroxyl, or water is associated. But, aside from this, in class A. I. a, “acidic” hydrogen, the dehydration temperature is likely to be relatively high; in A. I. b, “basic” hydrogen, somewhat lower; and in A. I. c, water of crystallization, relatively low, especially for the first water given off from a series of hydrates. In this case the water from two or more states of hydration may come off at one temperature unless the surrounding atmosphere has a carefully controlled and rather high-water content.

The escape of water from mix crystals is likely to be gradual as temperature increases, but experimental results are lacking.

Nonessential hydrogen is most likely to be given off continuously, but there are exceptions. For example, included water may escape discontinuously as the cavities containing it are burst open (decrepitation of the mineral); and even capillary water may escape more or less discontinuously if the heating changes the size of the pore spaces.

2. Heating with continuously increasing temperature, the water-vapor pressure being largely determined by the dehydrating substance.

The rate of loss of water as determined by frequent weighings² or by Le Chatelier’s method of heat absorptions is either discontinuous or continuous, about as stated in the preceding section, except

¹ Thermal dehydration may give some other hydrogen compound, HCl from $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, for example.

² Hillebrand, W. F., Merwin, H. E., and Wright, F. E., *Proc. Am. Philos. Soc.*, vol. 53, 1914, p. 45; *Zeitschr. Kryst.*, vol. 54, 1915, p. 221.

that the temperatures at which discontinuities occur are much influenced by such factors as rate of heating, state of subdivision of the material, and method of agitating the material during heating; the discontinuities themselves, however, tend to be more marked, especially in case of a series of hydrates.

3. Determination of vapor-pressure curves in cases of reversible changes in water content.

This determination gives very definite information concerning the state of hydration of a substance, but it is not commonly made as an analytical procedure.

C. EFFECT OF DEHYDRATION ON PHYSICAL PROPERTIES.

In general the crystallographic, optical, and other properties are likely to be profoundly changed by dehydration when the hydrogen is essential, and but slightly changed when it is nonessential. There are here, however, as in most other phenomena, important exceptions to the rule. In particular, some of the zeolite minerals, in which the water is presumably in part essential, may show only minor changes in their properties when they are partly or even completely dehydrated. In minerals of class A. II, also, the change in properties incident to loss of water may be but slight. On the other hand, when minerals contain considerable quantities of nonessential water, marked changes in properties may result upon its removal.¹

d. CONCLUSION.

From the foregoing discussion it is evident that while determination of the condition of hydrogen in minerals is by no means a simple matter, considerable information upon it may be obtained by appropriate analytical procedure. No conclusions should be drawn from single observations, but when the results of several methods of study show converging indications, it is quite possible to decide, for the majority of minerals, the condition in which their hydrogen is present.

B. WATER TAKEN UP OR LOST ON GRINDING.

Before considering methods of determining water attention must again be called to the effect of fine grinding of mineral powders on their ability to take up from the air and retain at temperatures far above 100° very appreciable amounts of water, even in excess of 1 per cent. (See p. 60.) The following table contains typical data on this subject. For fuller details see the paper already cited.²

¹ Larsen, E. S., and Wherry, E. T., Jour. Washington Acad. Sci., vol. 7, 1917, pp. 178, 208.

² Jour. Am. Chem. Soc., vol. 30, 1908, p. 1120; Chem. News, vol. 98, 1908, pp. 205, 215.

Water content of powders of varying fineness, ground in air.

No.	Material.	Condition.	Water.	
			Below 100°.	Above 100°.
			<i>Per cent.</i>	<i>Per cent.</i>
1a	Diabasic norite or gabro.	<60 meshes to 1 cm.....	0.03	0.66
1b		Ground 30 min.....	.10	.66
1c		Ground 120 min.....	.74	1.00
2a	Altered basaltic greenstone.	<40 meshes to 1 cm.....	.22	3.13
2b		Ground 120 min.....	1.70	4.19
3a	Andesite.....	<60 meshes to 1 cm.....	1.01	3.40
3b		Ground 30 min.....	1.18	3.54
4a	Quartz.....	<60 meshes to 1 cm.....	None.	.06
4b		Ground 120 min.....	.35	.45
5a	Meerschaum.....	Coarse.....	5.76	6.79
5b		Ground 600 min.....	6.33	9.81
6a	Unglazed Berlin porcelain.	Coarse.....	None.	None.
6b		Ground (?) min.....	.62	.18

On the other hand, water of crystallization may be expelled from minerals by long-continued grinding. Thus the content in water of a specimen of gypsum was reduced from over 20 to about 5 per cent.¹ The inference is obvious that water of crystallization should be determined on unground material, if possible.

The following excerpt from the work of Day and Allen² on the feldspars, already cited, has direct relation to the above:

There is another error to which accurate specific-gravity determinations upon powdered minerals will be subject unless suitable precaution is taken. The exposure to the air during the period of grinding the samples gives opportunity for the condensation of sufficient atmospheric moisture upon the grains to affect the weight in air. The amount varies measurably with the size of the grains, as will be seen from the accompanying data, and probably with the degree of saturation of the atmosphere and the time of exposure.

Determination of moisture in 1 gram of powdered mineral upon exposure to the air.

[<=finer than. >=coarser than.]

Mineral.	Fineness (meshes to the linear inch).	Moisture.
		<i>Gram.</i>
Orthoclase (natural glass).....	<150.....	0.0006
Ab ₁ An ₅ (artificial glass).....	Selected, coarse.....	.0001
Ab ₁ An ₅ (artificial crystal).....	<100>120.....	.0010
Ab ₁ An ₁ (artificial glass).....	<100>120.....	.0007
Ab ₁ An ₁ (artificial crystal).....	<100>120.....	.0010
Ab (natural crystal).....	Coarse.....	.0006
Do.....	<150.....	.0009
Orthoclase (natural crystal).....	<120>150.....	.0011
Orthoclase (same sample).....	<150.....	.0031
Do.....	Still finer.....	.0059
Orthoclase (artificial glass).....	Everything>100.....	.0065
Orthoclase (portion of same).....	>150.....	.0022

¹ Jour. Am. Chem. Soc., vol. 30, 1918, p. 1120; Chem. News, vol. 98, 1908, pp. 205-215.

² Pub. Carnegie Inst. Washington No. 31, pp. 56-67; Am. Jour. Sci., 4th ser., vol. 19, 1905, p. 93. Consult also Mauzelius, R., Sveriges geol. Undersökning, Arsbok 1, 1907, No. 3; and Hillebrand, W. F., Jour. Am. Chem. Soc., vol. 30, 1908, p. 1120; Chem. News, vol. 98, 1908, pp. 205, 215; and the footnote on p. 50 of the present volume.

In the last two groups note that the moisture in graded portions of the same sample varies with the fineness.

We also verified the conclusion of Bunsen¹ that this absorbed moisture is not altogether removed at temperatures only slightly above 100° but requires 600° to 800°—equivalent to low red heat. Several samples for which the moisture had been determined were laid away in corked test tubes for a number of weeks, after which redetermination gave exactly the former value.

It is worth noting in this connection that these measured quantities of absorbed water are of the same order of magnitude as those usually obtained for the water content in feldspar analyses, where, again, of course, the finer the sample is ground for the analysis the greater the possible error from this cause. It may be that a part and occasionally all of the moisture usually found in these analyses is absorbed and the significance of its presence there mistaken.

C. IMPORTANCE OF EMPLOYING AIR-DRY POWDER FOR ANALYSIS.

The time-honored custom of drying a powdered specimen before bottling and weighing has long seemed to me one that has no sound basis in reason. Its object is plain, namely, that of securing a uniform hygroscopic condition as a basis for convenient comparison of analytical results, because some rock powders contain more hygroscopic moisture than others and the amount is dependent further on the degree of fineness of the powder. Nothing, however, is more certain than that by the time the dried substance is weighed it has reabsorbed a certain amount of moisture, small, indeed, in most cases, but very appreciable in others; and, further, that with every opening of the container tube moisture-laden air enters and is inclosed with the remainder of the dry powder. Therefore it may very well happen that a powder which has been dried will, after several openings of the tube, especially at considerable intervals, be nearly as moist as it was at first. Dittrich has expressed views similar to the above. Of course, it is understood that no deliquescent substance is present.

It is preferable to weigh the air-dry powder and to make a special determination of moisture. If all the portions necessary for an analysis are weighed out one after another, or even at different times on the same day, the error due to difference of hygroscopicity in dry and moist weather, which for most of the separate portions is an entirely negligible quantity, is eliminated. Only in the main portion, in which silica and the majority of the bases are to be estimated, can it ever be an appreciable factor. Especially is this true if a rather coarse powder is employed, such, for instance, as passes a sieve of 30 to 60 meshes to the linear centimeter. In many powders of this grade the moisture will fall below 0.1 per cent, whereas in those that have been ground for one to two hours it may easily exceed 1 per cent.

¹ Wiedemann's *Annalen*, vol. 24, 1885, p. 327.

D. ARGUMENT IN FAVOR OF INCLUDING HYGROSCOPIC WATER IN THE SUMMATION.

The question has been asked: "If the so-called hygroscopic water is not always such, but not infrequently includes essential water, why are not its separate determination and entry in the analysis unnecessary? Why make a distinction which after all may not be a true one?" The question involves the further consideration of the need in any event of including the loss at 100° or 110°.

It would seem to be a reasonable desire on the part of petrographers to have all analyses referred to a moisture-free basis in order that they shall be strictly comparable. This involves the omission of the "hygroscopic" water from the list of constituents, which would be eminently proper were it always possible to be sure that the loss at 100° to 110° truly represents such water. As it very often represents more, and the determination as to whether or not it does in each case is not always possible and would add to the time required for the analysis, it seems necessary to include this water. What errors may arise from its exclusion the following rather extreme case well illustrates: Certain rocks of Wyoming in powder form lost from 1 to 2 per cent of moisture at 110°. That not even an appreciable fraction of this was truly hygroscopic is fully demonstrated by the fact that the uncrushed rocks lost the same amount; yet the rule followed by many chemists and petrographers would have involved the removal of all this water as a preliminary to beginning the analysis, and not only would a most important characteristic have passed unnoticed, but the analyst would have reported an incorrect analysis, inviting false conclusions and possibly serious confusion. (See also second paragraph of footnote, p. 50, and examples cited on p. 75.)

Hence it may be said that the estimation of the loss at 100° or 110° and its separate entry in the analysis are advisable as affording to the lithologist an indication of the mineral character of one or more of the rock constituents, thus perhaps confirming the microscopic evidence or suggesting further examination in that line. A marked loss in weight at 100° by a coarse powder other than that of certain igneous glasses may be taken as almost positive proof of the presence of zeolites or other minerals which characteristically contain loosely held water. It has been objected that the hygroscopic moisture varies with the degree of comminution of the sample and with the condition of the air at the time of weighing, and that therefore it should not be incorporated in the analysis, but this variation is ordinarily not at all great if the powder is coarse.

5. WATER—METHODS OF DETERMINATION.

With the coarse powders that are needed to afford a true value for the hydrogen content of rocks and minerals, one or another of the methods described in this section will be found more or less unsatisfactory, especially with those materials that lose their hydrogen at very high temperatures or that are difficult to decompose with fluxes. Unfortunately at present no directions can be given to cover all such cases. The analyst must exercise judgment in the selection of a method. In any event duplicate determinations should be made until he has acquired the experience that will permit him sometimes to make exceptions. M. Dittrich¹ has compared different ignition methods.

A. INDIRECT METHODS.

a. GENERAL CONSIDERATIONS.

The means employed for the indirect determination of water differ according as fractional or total amounts are needed. For the latter simple ignition is adopted; for the former exposure to the effects of dehydrating reagents or different temperatures. These methods, as ordinarily carried out, while exceedingly simple, are affected in most cases by serious errors, which will be considered in turn in their proper places: The methods should not be employed, therefore, when accuracy is essential, unless it is known that the errors are too slight to be significant or unless modifications are introduced to guard against them. A complication, sometimes serious, is added by the fact that with coarse powders the time required for expulsion of the water may be much greater than when a fine powder is used.

b. METHODS INVOLVING THE USE OF DEHYDRATING AGENTS.

Calcium chloride, sulphuric acid, and phosphorus pentoxide are the chemical dehydrants commonly employed in mineral analysis. Of these sulphuric acid finds most extended use, generally in a condition of high concentration, but in varying degrees of known concentration if detailed study of the behavior of a mineral during dehydration is in progress. I have shown² the importance of employing in desiccators only sulphuric acid of maximum dehydrating power when the full effect of the acid is desired. That which has stood long in desiccators that are in constant use is by no means so effective as fresh strong acid. Furthermore, the acid becomes dark from access of organic matter from dust or from the lubricant of the vessel, and this gives rise to the formation of appreciable amounts of sulphur dioxide.

¹ Zeitschr. anorg. Chemie, vol. 78, 1912, p. 191.

² Am. Chem. Jour., vol. 14, 1892, pp. 6-7.

A mineral which loses much water over a strong dehydrant may need an exposure of several days or even weeks for its complete extraction. If the weighings are made from day to day, the apparent limit may be reached long before all water really removable has been taken up by the acid. Whenever the crucible, after weighing, is replaced in the desiccator it is no longer in a dry but a more or less moist atmosphere, and its contents, even when covered, sometimes absorb a part of this moisture and retain it so persistently that the acid is unable to bring the powder beyond its previous state of dryness in the next 24 hours. In fact, it may be unable even to reach it unless greater time is allowed. An experiment on tyrolite, made and published many years ago, illustrates this point in part:

Experiment of drying 1 gram of tyrolite over strong sulphuric acid.

Time exposed.	Loss.	Time exposed.	Loss.
<i>Hours.</i>	<i>Gram.</i>	<i>Hours.</i>	<i>Gram.</i>
18	0.0231	24	0.0002
26	.0083	24	.0003
23	.0029	48	.0006
24	.0012	24	.0002
23	.0008		
24	.0001	283	.0380
25	.0003		

The experiment might reasonably have been considered ended after the 138th hour, when a loss of but 0.1 milligram was shown during 24 hours; but nevertheless a nearly steady loss of 0.3 milligram per day took place for six days more, and might have been observed longer but for the interruption of the experiment.¹ The sample was in fine powder. Had it been coarse, the rate of dehydration would have been much slower. The time can of course be greatly reduced by operating in a vacuum.

The indirect method can be made more accurate by heating the mineral or rock in a weighed tube, through which a current of air or other gas can be passed, either dry or of definite moisture content, according to the object in view, and then determining the loss in weight of the tube and its contents. If the drying agent for the gas is phosphorus pentoxide, it is well to cause the gas to pass first over or through calcium chloride or sulphuric acid, for the effectiveness of the pentoxide rapidly lessens as it becomes glazed with metaphosphoric acid.

C. METHODS INVOLVING THE APPLICATION OF HEAT.

a. Fractional determinations.—As to the temperature to be adopted for drying in order to determine so-called hygroscopic moisture, the

¹ Consult Mallet, J. W., Phil. Trans., vol. 171, 1830, p. 1006, for an example of slow loss of water from alum in air in an experiment lasting six months.

practice has varied at different times and with different workers, ranging from 100° to 110° . For the great majority of rock specimens it is quite immaterial which of these temperatures is adopted, for no greater loss is experienced at the higher than at the lower temperature, given a sufficient time for the latter. It is the practice in the Survey laboratory to employ a toluene bath giving a temperature of about 105° . Should the results show a very unusually high loss, the powder is reheated at, say, 125° , in order to learn if the loss is progressive with increased temperature, as this knowledge is important for the interpretation of results. To insure accuracy this experiment should never be made in crucibles or dishes which must be cooled in a desiccator. One instance will suffice: A gram of a mineral mixture containing about 17 per cent of water, of which about 3 per cent was driven off at 100° and 8 or 9 per cent at 280° , was placed in a desiccator over sulphuric acid, after several hours' heating at the latter temperature, and weighed as soon as cold, and then replaced and again weighed the next day. It had regained $1\frac{1}{2}$ per cent of its original weight, although the desiccator was tightly closed and the crucible covered, showing apparently a drying power superior to that of the acid, or having, in other words, a vapor tension less than that of the acid.

A specimen of tyrolite was found on one occasion to lose 10.34 per cent at 280° , and on another occasion 14.33 per cent. In the latter case the drying and heating at progressive temperatures had continued during a period of 528 hours, the weighings being made usually from day to day; whereas in the former the duration of the experiments was much shorter and the intervals between weighings were but a few hours each.

An important research of G. Friedel¹ well shows what errors are possible in the determination of this easily removable water, as he found that certain zeolites which had been largely dehydrated but not heated to the point of rupture of the molecular net could then absorb, instead of water, various dry gases in which they might be placed, as carbon dioxide, ammonia, carbon disulphide, and others, even air in large quantities, and certain liquids. In the light of this observation the cause of the great increase of $1\frac{1}{2}$ per cent in weight of the partly dehydrated mineral mentioned above may very possibly be attributed to air from the desiccator instead of moisture, as was at the time supposed. At any rate, as Friedel says, the danger of accepting a loss in weight as an index of the amount of water lost is clearly shown, and thus that method of determining water is for many cases fully discredited. Just what method to adopt must be left largely to the judgment of the operator, who will often be guided by the mineral

¹ Bull. Soc. min., vol. 19, 1896, pp. 14, 94; Compt. Rend., vol. 122, 1896, p. 1006.

composition of the rock as revealed by the unaided eye or the microscope.

Friedel indicates a means for determining the true weight of water lost by minerals behaving like the zeolites, even without collecting the water lost, namely, by driving out of the dehydrated and weighed mineral, under proper precautions, any air it may have absorbed in the process of drying and cooling, and collecting and measuring this air and thus finding its weight, which, added to the apparent loss, gives the true content of water.

But aside from the above reasons for avoiding the use of indirect methods of water determination, there is another very important one. They never give correct results where air baths are used in the ordinary way, for the reason that the drying is performed in an atmosphere far from dry, and therefore the substance can not lose all its moisture. As examples, if the indirect method shows 0.12 and 0.75 per cent in two samples, the direct method may afford 0.17 and 1.00 per cent, respectively. Similar observations have been repeated many times and admit of no dispute. They apply as well to rocks as to minerals. Therefore, if the moisture content is more than an insignificant factor the indirect method must be avoided or so arranged as to insure a constantly changing dry atmosphere.

To effect this the powder should be heated in a weighed tube, through which a current of dry air can be passed, and allowed to cool therein, after which a second weighing gives the loss of moisture. The degree of drying will depend on the nature of the reagent used for drying the air, sulphuric acid being more effective than calcium chloride, and phosphorus pentoxide most effective of all. When using the last, it is well to cause the air first to pass over or through one of the first-named dehydrants, for its effectiveness rapidly lessens as it becomes glazed with metaphosphoric acid. For experiments carried out at room temperature no bath is required, but for artificial temperatures the tube should pass through a suitable thermostat.

β. "*Loss on ignition*" method for total water.—In a few cases the simple loss on ignition of a rock will give the total water with accuracy, but in the great majority there are so many possible sources of error that this old-time method can seldom be used with safety. Only when the rock is free from fluorine, chlorine, sulphur, carbon, carbon dioxide, and fixed oxidizable or reducible (MnO_2) constituents can the loss be accepted as the true index of the amount of water present, and it is seldom that a rock is met with fulfilling these conditions, especially as to the absence of ferrous iron. Blast ignition in presence of carbon dioxide alone of the above list may give a correct result, after separate estimation of the carbon dioxide, provided this

emanates from carbonates of the earths and not from those of iron or manganese. Another source of error lies in the fact that from some minerals the hydrogen is not all driven out, even at the highest temperature obtainable by a blast lamp. Such heat may, on the other hand, drive out other difficultly volatile constituents, as the alkalies. This happens particularly when mixtures of alkaliferous silicates and alkaline-earth carbonates are concerned, such as argillaceous limestones.

The long-maintained idea that in presence of ferrous iron a sufficiently correct result is obtainable by adding to the observed loss an amount needed for oxidizing all ferrous iron is not justifiable. There can be no certainty that the oxidation has been complete, especially in the case of readily fusible rocks, and at the high temperature of the blast a partial reduction of higher oxides is not only possible but sometimes certain.¹ The inability to insure complete oxidation by simple ignition is illustrated in the case of precipitated ferric hydroxide which has been ignited in contact with its filter paper. If the quantity was in any degree large, it is sometimes decidedly magnetic, presumably from presence of magnetic oxide, which no amount of heating wholly oxidizes, especially in the larger grains. Neither is evaporation with nitric acid and reignition sufficient to destroy the magnetic property of the oxide, as has been claimed.

P. G. W. Bayly,² in a paper on recent methods of rock analysis, gives the following method for determining water. The total ignition loss is corrected for carbon dioxide when this is present, and for ferrous oxide by determining the ferrous iron both before and after ignition. Deduction of the separately determined moisture gives finally the more firmly held water. It need hardly be said that this method presupposes very exact determinations of both moisture and ferrous oxide.

B. DIRECT METHODS WITHOUT ABSORPTION TUBES—PENFIELD'S METHODS.

a. FOR MINERALS EASILY DEPRIVED OF THEIR WATER.

If no other volatile constituents than water are present, the beautifully simple method first used by G. J. Brush and extended by S. L. Penfield³ leaves nothing to be desired for accuracy, provided that the expulsion of water can be effected at relatively low temperatures. It consists simply in heating the powder in a narrow tube of hard glass, enlarged at the closed end and provided with one or two

¹ H. Warth (Chem. News, vol. 84, 1901, p. 305) also mentions this and draws attention to the effect of alumina, not only in decolorizing ferric oxide when the two are heated together, but also in restraining the reduction of the latter to the magnetic oxide.

² Australasian Assoc. Adv. Sci., Adelaide meeting, 1907.

³ Am. Jour. Sci., 3d ser., vol. 48, 1894, p. 31; Zeitschr. anorg. Chemie, vol. 7, 1894, p. 22.

further enlargements in the middle to hold the water and prevent its running back and cracking the hot glass. A capillary glass stopper fitted in with rubber tubing prevents loss of water by circulating air currents. The tube being held horizontally, the bulb is heated to any required degree by the Bunsen or blast flame. Moistened filter paper or cloth wound about the cooler parts of the tube insures condensation of all water. The heated end being finally pulled off, the tube is weighed after cooling and external cleansing, and again after the water has been removed by aspiration. For most rocks, as they contain little water, central enlargements of the tube are hardly needed.

Various forms of tubes used by Penfield are shown in figure 11.

Before using, even if apparently dry, "these tubes must be thoroughly dried inside, which is best accomplished by heating and

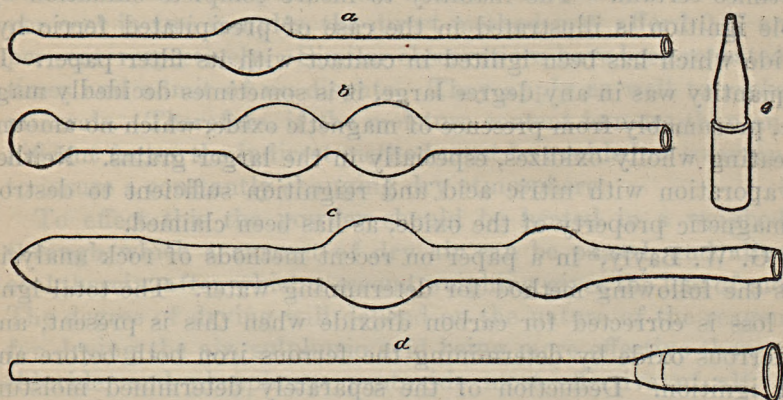


FIGURE 11.—Penfield's tubes for water determination in minerals. *a*, *b*, *c*, Different forms of tubes; *d*, thistle tube for introducing the powder; *e*, capillary-tipped stopper.

aspirating a current of air through them by means of a glass tube reaching to the bottom."

How this simple tube is made to afford entirely satisfactory results with minerals, even when carbonates are present, is fully set forth in the paper cited.

Comparatively few rocks are altogether free from other volatile constituents. Hence for refined work the application of this apparatus in the simple manner above set forth is limited. However, it may be used with the addition of a retainer for fluorine, sulphur, etc., such as the oxide of calcium, of lead, or of bismuth. It gives, of course, the total water.

B. FOR MINERALS NOT EASILY DEPRIVED OF THEIR WATER.

When minerals are present that do not give up their water wholly, even over the blast, as talc, topaz, chondrodite, staurolite, Penfield

recommends the use of the simple combination of fire-brick and charcoal oven, which is depicted in figure 12, either with or without a retainer in the tube for fluorine, as circumstances demand. The part of the tube in the fire is to be protected by a cylinder of platinum foil tightly sprung about its end, and the part outside by asbestos board, as well as by wet cloth or paper. A piece of charcoal is likewise laid on the tube, as well as beneath and behind, and the blast flame is given a horizontal direction, so as to play upon the side of the apparatus. In this way a most intense temperature can be reached, but the platinum foil does not last long.

M. Dittrich¹ condemned the above method as giving variable results, after comparative trial of different methods, but it would seem that he did not use a retainer for fluorine or sulphur.

In whichever way the apparatus may be used the water found is the total water, from which that found separately at 105° may be deducted if desired.

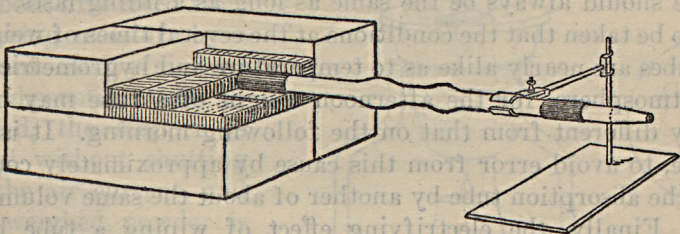


FIGURE 12.—Penfield's fire-brick and charcoal oven for use in determining water.

C. DIRECT METHODS WITH ABSORPTION TUBES.

a. GENERAL CONSIDERATIONS.

In general it is preferable to collect and weigh the water in suitable absorption tubes after its expulsion from the rock or mineral. The method is especially suited for the determination of total water or of that escaping above 105° when the apparatus of Gooch (f, p. 85) or of Dittrich and Eitel (e, p. 84) is employed. It is less suited for those fractional determinations where the escape of water is very slow at the different temperatures, for the absorption tube in such cases may gain weight, other than that of water from the mineral, sufficient to introduce appreciable error. This may sometimes be corrected to a certain extent by running a parallel blank test.

Absorption, following ignition without a flux, is not suited for rocks or minerals which yield other volatile substances than water and carbon dioxide, unless some substance is employed to retain these before they pass into the absorption tube. Even so, at extreme

¹ Zeitschr. anorg. Chemie, vol. 78, 1912, p. 191.

temperatures the results are likely to be in error, so that for materials which yield their water only at very high temperatures fusion with a flux is imperative.

A precaution too often overlooked is to see that the drying agent used for the air current (always forced, not drawn) is the same as that in the absorption tube in which the water from the sample is collected—not only the same in kind, but as near as may be in strength also, especially with calcium chloride. Therefore the contents of drying and absorption apparatus should be changed often, and when the apparatus is refilled the reagents should be taken from the same stock. Fresh calcium chloride in absorption tubes should be exposed to a current of carbon dioxide and the excess removed by air before use. Furthermore, all connections should be as nearly as possible glass against glass, with the least possible inside exposure of rubber. With long rubber connections the error may be a very sensible plus one. Again, the direction of the air current through the absorption tube should always be the same as long as a filling lasts. Care must also be taken that the conditions at the several times of weighing of the tubes are nearly alike as to temperature and hygrometric state of the atmosphere, for the afternoon weight of a tube may be appreciably different from that on the following morning. It is well, therefore, to avoid error from this cause by approximately counterpoising the absorption tube by another of about the same volume and weight. Finally, the electrifying effect of wiping a tube before placing it on the balance must not be overlooked. In my experience this has often amounted to as much as 1 to 2 centigrams in a balance resting on glass (always an increase in weight) after wiping with a clean linen handkerchief. The charge can be removed by repeated application of the hand, but disappears slowly without such aid. A strongly electrified condition makes itself apparent by marked irregularities in the swing of the needle. While more pronounced in cold weather, the phenomenon is not peculiar to winter.¹

The absorption tubes should not weigh in general over 30 grams each, filled with calcium chloride. Those preferred by me are shown in figure 14 (p. 82), and are 10 to 11 cm. over all in height. Sulphuric acid as an absorbent has no apparent advantage over calcium chloride if the drying apparatus for the air contains also calcium chloride of the same absorptive power as that in the collecting tube.

The methods of P. Jannasch that were given in preceding editions of this work are omitted here because of the error introduced by the taking up of water during grinding of the sample to the excessive fineness which the methods call for.

¹ With regard to electrification, consult also Bornemann, Ernst, *Chem. Zeitung*, 1908, pp. 125, 220.

D. STEIGER'S APPLICATION OF THE TOLUENE OVEN (FOR LOW TEMPERATURES).

The apparatus devised by George Steiger consists simply of a U-tube of home construction and a small toluene oven, in the cover of which is an opening of suitable shape to receive the tube (fig. 13). The open space between the uprights is closed when in operation by a piece of asbestos board. The horizontal end of the tube is made long, so that in the event of much water being given off it can be readily driven over into the absorption tube by a low flame, which if applied from the first may prevent any appreciable condensation of water before reaching the calcium chloride. The interior of the tube having been first freed from adhering moisture by a current of dry air and the absorption tube attached, the stopper is lifted without shutting off the air current, and the weighed powder is quickly introduced by means of the clean metal trough in which it has been weighed (fig. 4, p. 35). The stopper is replaced as quickly and the dehydration begins at once and often is nearly finished by the time the thermometer indicates the maximum temperature.

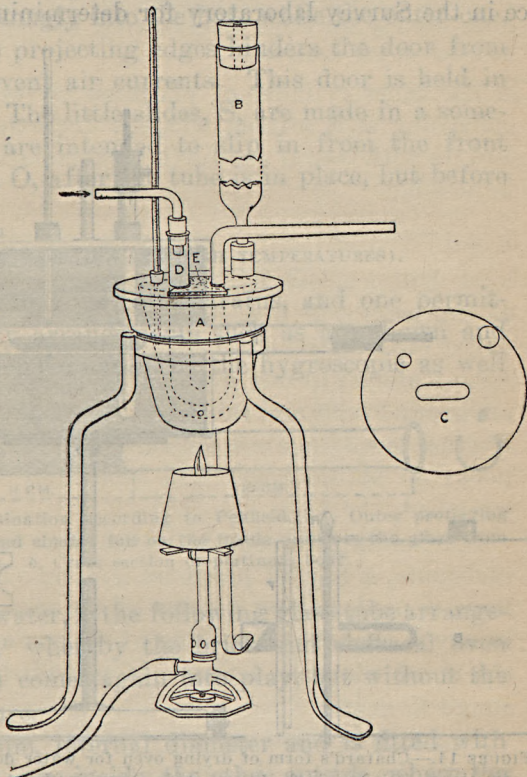


FIGURE 13.—Steiger's form of drying apparatus. A, Toluene oven; B, condenser, about 50 cm. high; C, cover of bath, showing openings; D, tube for mineral powder; E, asbestos board cut so as to close central opening in cover.

If the sample has no easily oxidizable constituents, it would be quite possible, by employing a U-tube with glass stoppers, like A, figure 14, page 82, to ascertain the loss in weight of the powder as well as the gain of the absorption tube, or to do away with the tube altogether. In this case, however, it would be necessary to vaseline the stoppers very lightly, and perhaps to introduce the powder through a dry funnel because of the vaseline film on the inner side of the end of the tube. The moderate heat on the top of the bath would suffice to prevent condensation of moisture before

reaching the absorption tube, or to soon remove what might condense at first, but there must be no long rubber connections.

By employing a suitable oven this form of tube can be used for higher temperatures, but the stoppers must fit air-tight, for vaseline can not be employed.

C. CHATARD'S OVEN FOR TEMPERATURES UP TO 300° AND OVER.

A form of drying oven devised by T. M. Chatard¹ gave good service in the Survey laboratory for determining water at different tem-

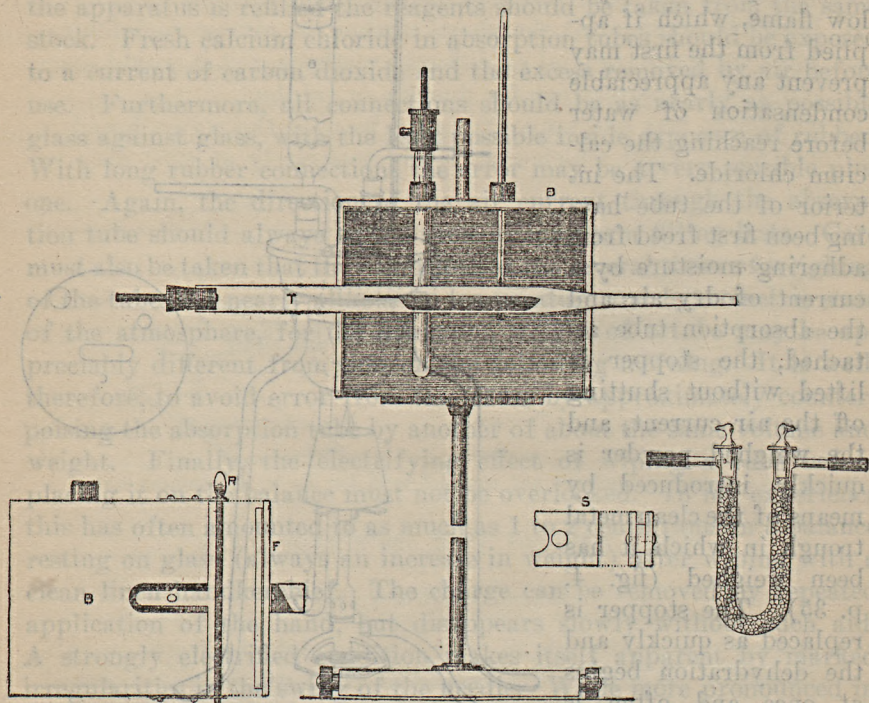


FIGURE 14.—Chatard's form of drying oven for water determinations. B, Copper box, 18 cm. long, 10½ cm. high, 9 cm. wide, open in front, its sides and top covered with asbestos board; S, two slides of different sizes to close openings, O, after the tube is in position; F, asbestos-board front stiffened by an interlaid sheet of copper; R, metal rod to hold front in place; T, glass ignition tube; A, calcium-chloride absorption tube. For mineral substances with very high water content the tubes T and A may preferably have the original form given them by Chatard, as depicted in Bulletin 176, p. 37. The use of a straight tube, as shown above, permits a less complicated construction of box and stand than that here shown, as round holes in opposite ends of the box admit the ignition tube, and the roller base is then superfluous.

peratures up to 350°. It is an asbestos-covered copper box shown in different aspects and parts in figure 14. The box is so constructed that the tube with its contents can be removed without detaching from either the drying or collecting tubes, which is a great advantage if it is desired to apply afterward the direct heat of a lamp in order

¹ Am. Chem. Jour., vol. 13, 1891, p. 110; Bull. U. S. Geol. Survey No. 78, 1891, p. 84.

to expel the water retained at 300° to 350° . To facilitate this removal the stand is on rollers, so that after clamping the projecting end of the tube and removing the front of the box, F, and the little side pieces, S, closing the horizontal slits, the oven can be rolled bodily backward, leaving the tube and its attachments in their original position, ready for further heating over a burner or blast. The removable front, F, of the oven is made of two pieces of sheet asbestos board stiffened by an interlaid piece of sheet copper. The inner piece of asbestos board fits snugly into the box, while the outer one, being slightly larger, by its projecting edges hinders the door from falling in and helps to prevent air currents. This door is held in place by the metal rod, R. The little slides, S, are made in a somewhat similar manner, and are intended to slip in from the front and close the two openings, O, after the tube is in place, but before closing the front.

d. PENFIELD'S PROCEDURE (FOR LOW AND HIGH TEMPERATURES).

The simplest of these methods as to apparatus, and one permitting, by the use of auxiliary arrangements such as are shown and described on page 82, the determination of the hygroscopic as well

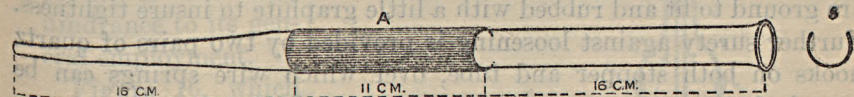


FIGURE 15.—Tube for water determination according to Penfield. A, Outer protecting covering of platinum foil. A second similar foil on the inside prevents the glass from collapsing when heated to softness. b, Cross section of platinum boat.

as any other fraction of the water, is the following glass-tube arrangement (fig. 15) of Penfield,¹ whereby the brick and charcoal oven already referred to (fig. 12) comes again into play, but without the half brick shown in that figure.

The tube is of about 15 mm. internal diameter and is fitted with two platinum cylinders at A, one inside, the other outside, where the heat exposure is to be most intense.

These are made from pieces of platinum foil, about 0.07 mm. in thickness and 8 by 11 cm. in size, which have been previously bent around glass tubes of such a diameter that when applied to the combustion tubing the spring of the metal will hold them in place. A large platinum boat, 7 to 8 cm. long and 11 to 12 mm. in diameter, with a cross section like b, should be used, since this will readily hold a gram of mineral mixed with 5 grams of sodium carbonate. * * * The tube is placed in the angle formed by the charcoal lining, some pieces of charcoal are placed at the sides in front, leaving an opening through which the flame may be directed, and an additional piece is laid on top. The tube can readily be brought to a full white heat, and by forcing a slow current of dry air through the apparatus the carbon dioxide

¹ Am. Jour. Sci., 3d ser., vol. 48, 1894, p. 37; Zeitschr. anorg. Chemie, vol. 6, 1894, p. 22.

resulting from the decomposition can be removed and the water carried over into the weighed absorption tube. The glass fuses between the platinum casings, and in a number of experiments that have been tried there has not been a single instance where the glass tube has broken or shown any indication of breaking. After heating, the tube will not crack if it is left to cool slowly on the charcoal, but it can not be used a second time. * * * At the high temperature to which the glass is subjected it of course becomes very soft and the ends must be properly supported; also the rubber connections and absorption apparatus must be carefully screened by asbestos board. By constructing a cover for the boat no material need be lost by splattering, and after making the water determination the contents may be used for the remainder of the analysis.

The inner cylinder of platinum serves to prevent the glass from collapsing as it softens, whereby distortion of the boat would result and its withdrawal for further examination of its contents would be impossible.

e. DITTRICH AND EITEL'S APPARATUS (FOR LOW AND HIGH TEMPERATURES).

M. Dittrich and W. Eitel¹ recommend a tube of fused quartz of 45 cm. length, 22 mm. diameter, and 0.5 mm. wall thickness, drawn out at the exit end and provided with a stopper and inlet tube of the same material in one piece. The stopper and end of the large tube are ground to fit and rubbed with a little graphite to insure tightness. Further surety against loosening is provided by two pairs of quartz hooks on both stopper and tube, over which wire springs can be stretched.

For holding the sample, mixed with 5.5 to 6 grams of dry sodium carbonate, a boat of platinum-iridium (10 per cent iridium), 12 cm. long, is used, having a cover of the same alloy. To protect against injury to the tube by spilling of the contents of the boat a cylindrical shield of platinum-iridium is provided. Boat, cover, and shield weigh 42 grams.

Fusion is brought about by the heat of a row of burners, increased toward the end of the operation by that of a large blast lamp. An electric resistance furnace is preferred to gas as a source of heat. The temperature for complete fusion is 1,000° to 1,050°.

In a later paper² Dittrich and Eitel describe the determination of water and carbon dioxide simultaneously, without flux, in a similar apparatus but at higher temperatures (up to nearly 1,400°). The tube, however, is of platinum-iridium and of much smaller bore than that used with the flux. The boat is also smaller than the one described above, as it has to hold only the rock or mineral powder. For the purpose of retaining sulphur, fluorine, etc., a spiral of silver, 4 to 5 cm. long, is held at the exit end of the tube just before it narrows.

¹ *Zeitschr. anorg. Chemie*, vol. 75, 1912, p. 373.

² *Idem*, vol. 77, 1912, p. 365.

In view of the cost of the apparatus and the possibility of error arising from volatile constituents other than carbon dioxide and water, the use of this apparatus offers no advantages over the less expensive one before described, especially as carbon dioxide can be determined easily in a separate sample by another method.

f. GOOCH'S APPARATUS (FOR HIGH TEMPERATURES).

Of more elaborate apparatus, designed to be used with fluxes, the tubulated platinum crucible invented by F. A. Gooch¹ is capable of affording most excellent service, and it is the one by which far the larger number of water determinations have been made in the Survey laboratory. Its high cost, which puts it beyond ordinary reach, is the only hindrance to its general employment.

Figure 16, which hardly needs detailed description, shows it in a modified form, which differs from the original forms of Gooch in that the tubes for connecting with both the drying and absorption vessels are constructed wholly of platinum instead of lead glass. With inlet and exit tubes of the lengths shown in the figure there is absolutely no danger of the ends becoming hot enough by conduction to scorch or soften the rubber connection.

As an adjunct to its convenient use there is needed an ordinary upright iron ring stand, with two small sliding rings, and a sliding ring burner provided with entering ducts for gas and air blast. Across the uppermost ring there is an arrangement of stout platinum wire (S, fig. 17), forming at the center of the ring a secure seat for

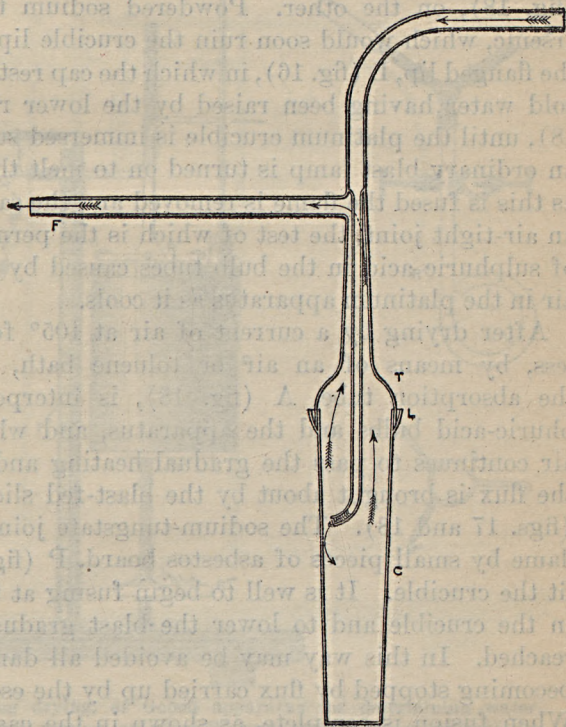


FIGURE 16.—Modified form of Gooch tubulated platinum crucible for the determination of water, one-half natural size. Weighs about 75 grams.

¹ Am. Chem. Jour., vol. 2, 1880, p. 247; Chem. News, vol. 42, 1880, p. 326.

the upturned flange of the crucible proper. Both rings and burner can be clamped firmly at any height.

The rock powder, having been placed in the cylindrical crucible (C, fig. 16), is there mixed with not more than 3 or 4 grams of fully dehydrated sodium carbonate,¹ or more of lead chromate if carbon is to be likewise determined. The crucible is sunk in its seat, S (fig. 17), in the upper ring, R', and the tubulated cap, T (fig. 16), is fitted on and attached to the calcium-chloride drying towers—preceded by one containing potassium hydroxide if carbon dioxide is likewise to be estimated—on the one side, and to a sulphuric-acid bulb tube, B (fig. 18), on the other. Powdered sodium tungstate²—free from arsenic, which would soon ruin the crucible lips—is now poured into the flanged lip, L (fig. 16), in which the cap rests, and a metal vessel of cold water having been raised by the lower ring, R'' (figs. 17 and 18), until the platinum crucible is immersed sufficiently, the flame of an ordinary blast lamp is turned on to melt the tungstate. As soon as this is fused the flame is removed and the salt solidifies and makes an air-tight joint, the test of which is the permanence of the column of sulphuric acid in the bulb tubes caused by the contraction of the air in the platinum apparatus as it cools.

After drying by a current of air at 105° for two hours, more or less, by means of an air or toluene bath, as shown in fig. 17, the absorption tube, A (fig. 18), is interposed between the sulphuric-acid bulbs and the apparatus, and while a slow current of air continues to pass the gradual heating and subsequent fusion of the flux is brought about by the blast-fed sliding ring burner, R''' (figs. 17 and 18). The sodium-tungstate joint is shielded from the flame by small pieces of asbestos board, P (fig. 18), cut out so as to fit the crucible. It is well to begin fusing at the top of the mixture in the crucible and to lower the blast gradually till the bottom is reached. In this way may be avoided all danger of the outlet tube becoming stopped by flux carried up by the escaping carbon dioxide. When fusion is complete, as shown in the case of sodium-carbonate flux by the decided slackening of the gas current through the safety bulbs attached to the drying tube, the flame is extinguished and a current of air is allowed to continue until the apparatus is cold.

This apparatus suffers from the drawback of being slightly permeable to combustion gases at high temperatures. The defect can be

¹ This has been heated for a length of time to near its fusing point over a free flame or in an air bath, to decompose the bicarbonate it usually contains, and then placed in a desiccator. Thus heated it is not very hygroscopic. Penfield found that 2.5 grams of it, spread out on a watch glass, gained only 0.0002 gram in 15 minutes. Potassium carbonate and potassium-sodium carbonate are too hygroscopic by far to be available.

² Private advice from E. W. Morley conveys the information that sodium carbonate is perfectly satisfactory as a substitute for the tungstate. If so, its use is preferable when the contents of the crucible are to be used for other determinations.

overcome by causing the flame to play upon an outer ordinary platinum crucible, kept permanently filled with sodium-potassium carbonate. This protective crucible, however, is soon ruined for other purposes, being distorted by the alternate expansion and contraction of the carbonate, unless this is poured out before it solidifies after each fusion.

It has been found that if the operation is carried out expeditiously and the final full heat applied for but a few minutes, the error due to

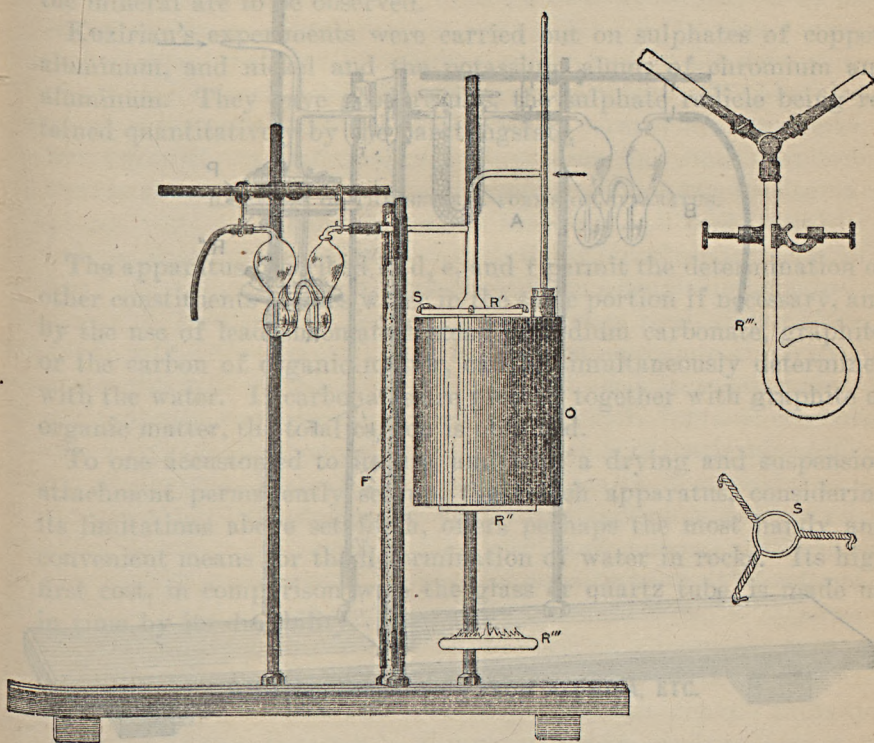


FIGURE 17.—Arrangement, during drying, of Gooch apparatus for determining water. S, Seat of stout platinum wire resting on ring R' and serving as a support for the crucible; R''', blast-fed ring burner; R'', support for air or toluene bath; O; F, asbestos-board shield.

penetrating water gases is inappreciable. This hastening may be rendered safer by using rather finely powdered calcium chloride in the central section of the U-shaped absorption tube to avoid large air channels. Through this or any other apparatus based on similar principles the air current should always be forced, not drawn. A warm air blast directed upon the exit tube near its entrance into the absorption tube greatly shortens the time required and is to be recommended.

In this apparatus only the water expelled above 100° to 110° should be determined as a rule. The reason why it is unsafe to attempt to determine "hygroscopic" moisture in this apparatus is that the luting of the two parts must be done by direct application of a flame to the tungstate, and considerable water vapor may enter the apparatus and be retained in part by the dried sodium carbonate.

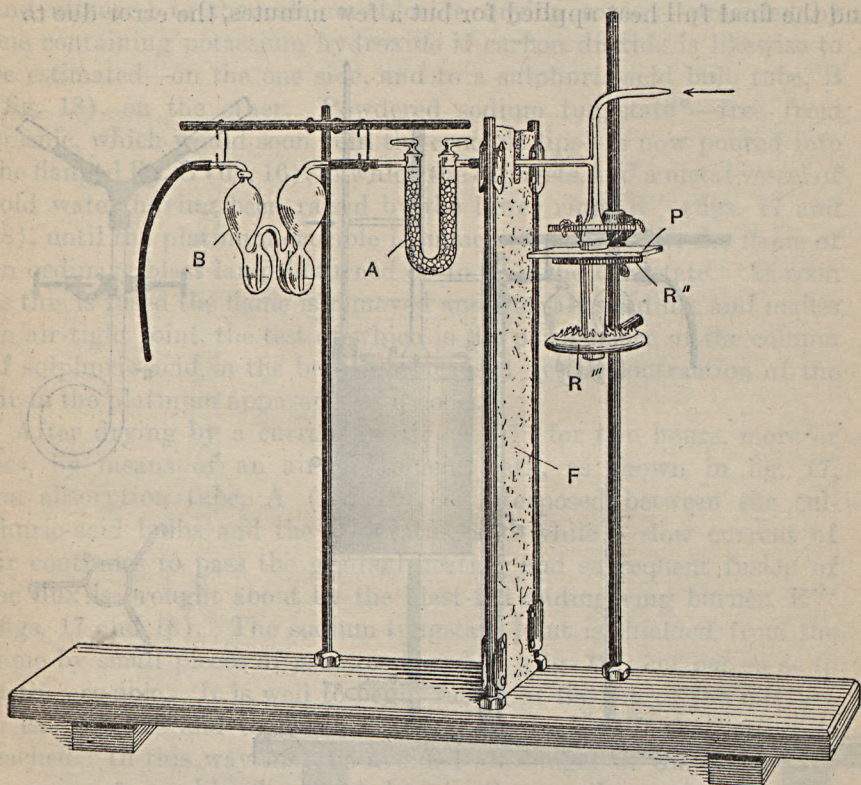


FIGURE 18.—Arrangement, during fusion, of Gooch apparatus for determining water. R''' , Blast-fed ring burner; P , protective asbestos shield resting on ring R'' ; F , asbestos-board shield; A , calcium-chloride tube; B , sulphuric-acid bulbs serving to show the rate of gas flow through the absorption tube and at the same time to prevent back entry of moisture from the air into A .

G. KUZIRIAN'S METHOD (FOR HYDROUS SULPHATES).

For the determination of water in those hydrous sulphates which are apt to lose some of their acid radical when heated S. B. Kuzirian¹ has developed a method which may find application for hydrous salts other than sulphates. An ignition tube, which may be of hard

¹ Am. Jour. Sci., 4th ser., vol. 36, 1913, p. 401; Chem. News, vol. 109, 1914, p. 173; Zeitschr. anorg. Chemie, vol. 85, 1914, p. 127.

glass, is used for heating the mineral. The sample is mixed in a boat of porcelain or platinum with six times its weight of sodium paratungstate¹ and inserted into the tube, which has been dried thoroughly by passing through it a rapid current of dry air. The ignition is started gently while dry air passes over the boat at a rate of three bubbles a second for 15 minutes. Then the temperature is increased gradually until the mixture forms a clear fusion. The usual precautions for drying the air and absorbing the water evolved from the mineral are to be observed.

Kuzirian's experiments were carried out on sulphates of copper, aluminum, and nickel and the potassium alums of chromium and aluminum. They gave good results, the sulphate radicle being retained quantitatively by the paratungstate.

H. MERITS OF THE SEVERAL FORMS OF APPARATUS.

The apparatus described in d, e, and f permit the determination of other constituents besides water in the same portion if necessary, and by the use of lead chromate instead of sodium carbonate, graphite, or the carbon of organic matter, can be simultaneously determined with the water. If carbonates are present, together with graphite or organic matter, the total carbon is obtained.

To one accustomed to its use, and with a drying and suspension attachment permanently set up, the Gooch apparatus, considering its limitations above set forth, offers perhaps the most handy and convenient means for the determination of water in rocks. Its high first cost, in comparison with the glass or quartz tube, is made up in time by its durability.

6. SILICA—SEPARATION FROM ALUMINA, ETC.

A. ALTERNATIVE METHODS OF DECOMPOSING THE ROCK.

a. GENERAL CONSIDERATIONS.

The almost universal practice in silicate analysis is to determine silica, titanium, and most of the basic elements in one and the same portion of the sample. The practice of separating alumina, etc., by the usual methods, after first attacking the rock powder by hydrofluoric and sulphuric acids—silica being estimated in a separate portion—while attractive in principle, was long ago abandoned by me after fair trial, owing to the disturbance sometimes occasioned by

¹ In order to purify the commercial paratungstate, which ordinarily contains sodium carbonate, it is fused in a large platinum dish over the blast, and pure tungsten trioxide is added until carbon dioxide ceases to bubble out.

incomplete expulsion of fluorine¹ and to a less degree by the presence of sulphates instead of chlorides. With the exception of a comparatively few analyses made thus the sodium carbonate method of attack has always been employed. In the case of rocks rich in fluorine strict accuracy requires the separation of silica to be made as in the Berzelius method for fluorine determination (see p. 226; also footnote, p. 93), but in practice it is not often necessary to resort to this tedious procedure, for the amount of fluorine is usually small and it could by no possibility cause a loss of much more than three-fourths its own weight of silica if it were all to volatilize as silicon tetrafluoride when the sodium-carbonate fusion is evaporated with hydrochloric acid. The loss is, however, less, as silicon fluoride is unstable in presence of moisture. Some of the fluorine escapes perhaps as hydrofluoric acid, and more is fixed in fluosilicates.² In any event the error is of comparatively slight importance, for it attaches always to the constituent that is present in greatest amount.

Various fluxes other than alkali carbonates have been recommended for breaking up silicates insoluble in ordinary acids, such as lead and bismuth oxides, lead carbonate, borax, and boric oxide. Jannasch and his pupils were especially active in this line of work. One of the advantages most of these fluxes possess over the alkali carbonates is their removability after serving their purpose, thus allowing the various separations to be made more perfectly and without the annoying interference of several grams of foreign fixed salts, which are most troublesome in that part of the analysis devoted to the separation of silica, alumina, iron, lime, and magnesia.

Another of their advantages is that with some of them it is possible to estimate in one portion the alkalies in addition to those constituents that are usually determined in the silica portion. Where the material is limited, as so often it is in mineral analysis, this is a most important advantage, sufficient to outweigh all possible objections; but in rock analysis, where the supply of material usually is ample, it is seldom worth considering. A still further point in their favor

¹ The presence of fluorine renders the precipitation of aluminum very incomplete. See also Veitch, F. P., *Jour. Am. Chem. Soc.*, vol. 22, 1900, p. 246; also Hinrichsen, F. W., *Ber. Deutsch. chem. Gesell.*, vol. 40, 1907, p. 1497; *Zeitschr. anorg. Chemie*, vol. 58, 1908, p. 83; and Cavaignac, H., *Compt. Rend.*, vol. 158, 1914, p. 948. The reason for the sometimes incomplete precipitation of aluminum by ammonia from sulphate solution, after attacking a rock by hydrofluoric and sulphuric acids, is ascribed by E. Selch (*Zeitschr. anal. Chemie*, vol. 54, 1915, p. 395) to incomplete removal of fluorine. He obtained complete recovery after a second evaporation with sulphuric acid, the first residue of sulphates being brought to a clear solution with dilute sulphuric acid before proceeding with the second evaporation. Contrary to some statements, Selch found that evaporation of alumina with hydrofluoric acid involves only a negligible loss by volatilization.

² A supposition confirmed by G. E. F. Lundell, at the Bureau of Standards. The fluosilicates, if eventually ignited with the silica, would undergo at least partial decomposition and on treatment of the ignited silica with hydrofluoric and sulphuric acids the metal of the fluosilicates (presumably sodium) would be weighed eventually as sulphate if not volatilized by the heat of ignition.

is that it is probably more easy to obtain them entirely free from fixed impurities than an alkali carbonate.

There are, however, objections to their use. With some of them an extraordinary amount of time must be devoted to grinding the mineral to an impalpable powder, with the result of introducing serious analytical complications. (See ante, p. 60.) And the flux itself may need considerable hand pulverization. Once introduced, they must be removed before the analysis can be proceeded with, and this removal takes much time and is always a possible source of error.

In mineral analysis these objections are entitled to far less weight than in rock analysis, for the object sought—usually the deduction of a formula—warrants the expenditure of much time and painstaking care. Finally, it has been found that one or more of these fluxes are not available for altogether general use, because certain minerals do not succumb fully to their attack under simple conditions, as andalusite with boric oxide and others with lead oxide (Jannasch). Therefore, however well adapted one or the other of these methods may be for the analysis of homogeneous minerals, the anticipations of Jannasch, to the effect that the boric-oxide method would soon supersede the alkali-carbonate fusion method in rock as well as in mineral analysis, have not been realized. Nevertheless the boric-oxide fusion method, owing to its evident merit, will be described in detail after brief reference to a means of bringing refractory silicates into solution without employing any solid reagent.

The methods of decomposition and the subsequent treatment of the silica hereinafter described are with few exceptions applicable to definite silicate mineral species as well as to complex mixtures of them.

b. DECOMPOSITION OF REFRACTORY SILICATES BY HYDROCHLORIC ACID UNDER PRESSURE.

Jannasch¹ pours upon the finely ground rock powder contained in a platinum tube of about 26 cm.³ capacity a somewhat diluted hydrochloric acid (4 acid to 1 water), places over the open end a cap which does not hermetically close the tube, inserts the latter in a larger tube of potash glass likewise partly filled with the diluted acid, seals the glass tube, places it in turn in an inclined position in a steel Mannesmann tube containing ether or benzine to equalize the pressure, and heats to any desired temperature up to 400°.

The chief drawback seems to be a somewhat incomplete decomposition, doubtless due to the necessarily inclined position of the tube, which causes the powder to collect at the lower end, and thus renders

¹ Ber. Deutsch. chem. Gesell., vol. 24, 1891, p. 273; Zeitschr. anorg. Chemie, vol. 6, 1894, p. 72.

decomposition less complete than if the material were spread evenly throughout the length of the tube. Further, the acid attacks the platinum strongly unless the air in both the platinum and the glass tubes is replaced by carbon dioxide. Even when this is done, several milligrams of platinum is found in the silicate solution.

Nevertheless, to those possessing the necessary platinum and steel tubes the method can render efficient service in special cases when economy of material is imperative.

C. THE BORIC-OXIDE METHOD OF JANNASCH AND HEIDENREICH.¹

a. Preparation of the boric oxide.—The boric-oxide method demands, if the alkalis are to be estimated in the same portion as silica, etc., an absolutely alkali-free boric acid, which can be prepared by two or three recrystallizations of a good commercial article. The purified crystals are dehydrated and fused in a large platinum crucible. This is then cooled suddenly to cause the anhydride to crack into pieces of a size convenient for powdering, which are to be kept in a tight glass vessel and powdered as needed, since the anhydrous oxide is hygroscopic.

β. Treatment of easily decomposable silicates.—To this flux Jannasch and Heidenreich found that nearly all silicates readily succumb over the ordinary blast lamp. The fusion is made in a large crucible holding 40–65 cm.³, and the proportion of flux to be used is gaged according to the nature of the silicate, ranging from 3 to 8 and more parts to 1 of mineral. This last must be finely powdered, especially if very resistant to attack by the flux, the authors recommending the expenditure of one-half to one hour's time for the grinding of one-half to 1 gram of powder. Heat from a burner turned low is applied for 5 to 10 minutes till water is expelled; the heat is then increased gradually till the gas is fully turned on. Bubbling and rising in the crucible is prevented as far as possible by using a short platinum rod which does not reach above the edge of the crucible. When the mass has been in quiet fusion for a time in the covered crucible the blast flame is applied. The average duration of the entire operation is 20 to 30 minutes but depends much on the character of the mineral.

γ. Treatment of refractory silicates.—For those minerals which, like andalusite, cyanite, and topaz, are not fully decomposable by the heat of the ordinary blast flame, P. Jannasch and H. Weber² used a

¹ Zeitschr. anorg. Chemie, vol. 12, 1896, p. 208. This method of decomposing rocks with a view to the determination of their contained alkali originated with Sir Humphrey Davy, as shown in his paper "On a method of analyzing stones containing fixed alkali by means of the boracic acid" (Phil. Trans., 1805, p. 231; Ann. d. chim., vol. 60, 1806, p. 294; Gilbert's Annalen, vol. 30, 1808, p. 369; Tulloch's Phil. Mag., 1806, p. 146). Original with Jannasch and Heidenreich is the manner of getting rid of the introduced boric oxide.

² Ber. Deutsch. Chem. Gesell., vol. 32, 1899, p. 1670.

flame fed by oxygen instead of air. The blast lamp, of 2½ mm. opening, is supplied with gas from at least five or six ordinary gas cocks, and the flame is made broad and free from luminosity. The mineral having been first heated as above described, but with a much larger proportion of flux—as high as 30 to 1—a few grams additional of boric oxide is added and the oxygen blast is applied till, in 10 or 15 minutes, the fusion is as transparent as glass.¹

2. *Further treatment after fusion.*—From this point the further treatment is the same in both cases and, as modified by Jannasch and Weber,² is as follows:

The hot crucible is cooled in cold water and the contents are turned into a very large porcelain or platinum dish, to which, after covering with a glass, a saturated solution of hydrochloric-acid gas in methyl alcohol is added.³ The cover being then removed, the liquid is heated to boiling, over asbestos board, by an inch-high flame, with constant stirring, or it is left without attention over a lower flame or on a water bath heated short of boiling. The crucible is cleansed in a similar manner, and its contents are added to the dish. In 10 to 15 minutes, with occasional addition of the methyl chloride, solution is complete and the liquid is then boiled down to a small volume and evaporated to dryness on the bath. The residue is then digested on a bath at 80° to 85° three or four times in succession with the ether solution, in order to remove the last traces of boron as boric ether. Care should be taken to wash down from the sides of the dish, with methyl-chloride solution, the boric acid formed and deposited thereon during the evaporation.

3. *Possible objections to the boric-oxide method.*—Very much was claimed by Jannasch for this method, but with all its undoubted merit there are several points which militate against it. (1) The boric ether, driven off in such quantities, at once decomposes in contact with moisture, and boric acid settles over all objects with which it comes in contact. The hood must become thickly coated. Hence a special hood for these evaporations alone seems to be called for, otherwise boric acid may at any time fall into other dishes and cause untold trouble. (2) The second objection attaches to the use of the oxygen flame when alkalies are to be estimated in the fusion, and the ability to so determine them is one of Jannasch's chief claims in favor of the method, for it can not be doubted that at the high temperature of this flame alkalies are volatilized. Borax can be volatilized slowly

¹ An interesting and important observation reported by Jannasch and Weber is that when the oxygen blast has been used for silicates carrying fluorine or mixed with fluorides the fluorine seems to be wholly expelled as boric fluoride without loss of silica. No verification of this by any one has been made up to the present (1919).

² Ber. Deutsch. chem. Gesell., vol. 32, 1899, p. 1670.

³ Made by passing dry hydrochloric-acid gas into cooled methyl alcohol for from one to two hours.

but wholly over the ordinary blast, hence there is great reason to fear sufficient loss at this much higher temperature to give rise to serious error. (3) Incomplete expulsion of the boric acid gives rise to errors later in the analysis.

d. THE SODIUM-CARBONATE METHOD.

α. Advantages of sodium carbonate over sodium-potassium carbonate.—Except in special cases, as when fluorine or chlorine are to be determined, there is no advantage in using the much recommended, because more fusible, double carbonate of sodium and potassium, or the equimolecular mixture of the normal carbonates, or of sodium carbonate and potassium bicarbonate. As Dittrich says,¹ potassium salts are more prone to pass into precipitates than sodium salts, and it may be that the higher melting point of sodium carbonate is a distinct advantage. Certainly, for effective decomposition of some rock constituents, a far higher temperature than that of the fusing point of the double salt is required.

β. Purity of the sodium carbonate.—Notwithstanding the most earnest efforts for years, it has been impossible to procure, either in the open market or by special arrangement with manufacturers, a grade of sodium carbonate which can be called chemically pure. With special precautions small lots can be prepared in the laboratory that will contain less than 1 mg. total impurity in 10 grams; but such an article can not be purchased in the market, and rarely will the so-called chemically pure dry sodium carbonate contain as little as 1 mg. in 10 grams. The invariable contaminating substances—aside from sand and straw, which have sometimes been found—are silica, alumina, iron, lime, magnesia, and sometimes phosphoric oxide, all of these going into aqueous solution with the carbonate. The chief of these impurities are usually silica, alumina, and lime. Sulphur can be found almost always in minute amount, but this is not objectionable for the present purpose. An article of the above degree of purity (1 mg. in 10 grams) is satisfactory in almost all imaginable cases, as the use of the usually extravagant amount of 10 grams for a fusion would introduce an error of but 0.1 per cent in the analysis, supposing 1 gram of mineral to be operated on, and it would, moreover, be distributed over several constituents. Undoubtedly this error is fully equaled by the introduction of dust from the air in the various long evaporations.

It is to be borne in mind that the so-called dry sodium carbonate, "C. P.," almost always contains some bicarbonate and hence yields water on heating. This, however, in no way detracts from its usefulness, and it is not necessary to convert it wholly to the normal salt

¹ Anleitung zur Gesteinsanalyse, 1905, p. 5.

for fusion of the kind now contemplated. In fact, C. Holthof¹ most strongly recommends using the bicarbonate itself as a flux instead of the normal carbonate. (See *z*, p. 96.)

γ. The fusion with normal sodium carbonate.—Ordinarily from 4 to 6 parts of the flux should be used to 1 part of rock powder, thoroughly mixed in a crucible of 20 to 30 grams weight. It is inadvisable to use the much larger proportion of flux recommended by some writers, except as it may be shown to be needed in isolated instances. The larger amounts introduce more impurity than the smaller and necessitate longer washing of precipitates. At first, the crucible (covered) is placed over a moderately low Bunsen flame, which is gradually increased to the maximum and maintained there till the mass is quiescent. There should be no violent action. The contents of the crucible will then appear, in the case of highly feldspathic or quartzose rocks, as a viscous liquid, occasionally almost clear, though generally more or less turbid, and when placed over the blast little or no further effervescence occurs. Melts of this character disintegrate very readily in water. With less siliceous rocks the fusion is less perfect and may be far from complete, though this does not necessarily imply incomplete decomposition of the silicates. It is generally advisable and often necessary to place these less fusible mixtures over the blast lamp, when a further and very marked escape of carbon dioxide takes place, and the crucible cover should be lifted cautiously at intervals to avoid loss by boiling over. This boiling is due not merely to further action of the carbonate on the rock-forming minerals, but oftentimes more to the decomposition of the alkaline earth carbonates, whose bases then enter into combination with other constituents of the flux and rock to form compound silicates and probably aluminates. It is a great mistake to regard, as many seem to have done, the alkaline-earth metals, magnesium, iron, and manganese as present in the form of carbonates after a blast fusion. They are rarely in that state even when only the Bunsen flame has been used.

The blast flame during fusion should not be directed vertically against the bottom of the crucible, but at an angle against the side and bottom, nor should the flame be allowed to envelop the whole crucible. These precautions apply in all ignitions of reducible substances, and yet they are too often neglected. In neither case, if neglected, will there be the necessary oxidizing atmosphere within the crucible; on the contrary, reduction may occur fraught with serious consequences. This is especially true if the rock contains more than traces of pyrite or other sulphide, when, after cleansing and igniting the crucible, there may appear on its interior a darken-

¹ Zeitschr. anal. Chemie, vol. 23, 1884, p. 499.

ing due to oxidation of reduced iron which had alloyed with the platinum. In exceptional cases this may amount to several milligrams in weight, and can be removed only by repeated ignitions, followed each time by scouring or treatment with hydrochloric acid or acid potassium sulphate. In order to avoid the use of niter in case of pyritiferous rocks, it is well to first roast gently the weighed powder in the crucible in which the fusion is to be made, turning the crucible around a few times to expose all of the powder to the air. With rocks exceptionally high in pyrite the roasting is done best in a porcelain crucible. In such case, after transferring the greater part to the platinum crucible, if brushing with a camel's hair brush does not remove the last of any adhering dust, scouring with a little sodium carbonate will be effective.

It is unsafe to make sodium carbonate fusions in a muffle. Tests made at the Bureau of Standards by E. Wichers with sodium carbonate by itself have shown a marked attack of the platinum above the melt, owing probably to the absence of an atmosphere charged with carbon dioxide and consequent formation of sodium hydroxide. This explains probably the conflicting statements that have been made regarding the effect on platinum of molten sodium carbonate.

It happens sometimes that the cooled flux, and even its solution, will indicate the absence of manganese when it is really present in quantity to give normally a strong coloration. Two fusions made side by side or successively, under apparently similar conditions, may in one case show little or no manganese, in the other considerable. This observation has been made frequently, and therefore the absence of a bluish-green color in the fusion is not to be taken as a proof of the absence of manganese. This difference of behavior I can ascribe to no other cause than that of a reducing atmosphere in one of the crucibles and an oxidizing one in the other, even though the conditions were apparently alike. It is, of course, not to be expected that the green color can show until all other oxidizable components of the rock, like sulphides, ferrous iron, and organic matter, have been fully oxidized, which, however, is soon the case if air has access to the surface of the melt.

2. *Fusion with sodium bicarbonate.*—C. Holthof,¹ who strongly recommends sodium bicarbonate as a flux, uses 12 to 15 parts of it to 1 part of the sample. One quarter of this is placed on the bottom of the crucible, a second quarter is mixed thoroughly with the rock powder in a small warmed dish, and the composite is then mixed with a third quarter on glazed paper and poured into the crucible. The last quarter is used for rinsing the dish and paper and covering the contents of the crucible, which may be half full. The crucible

¹ Zeitschr. anal. Chemie, vol. 23, 1884, p. 499.

is heated over a low flame till the bottom is dull red, then during 15 minutes the flame is increased till the lower quarter of the crucible is dull red, in which state it is maintained for 15 minutes. Then fusion is brought about by the full flame and maintained for a time. Holthof claims that action between the silicate and carbonate takes place at a lower temperature than with the normal carbonate before fusion, and that for this reason there is almost no spattering onto the lid of the crucible.

e. Treatment after fusion.—When fusion is complete, the crucible is seized with the tongs (fig. 1, p. 32), and the contents are caused to solidify in a thin sheet over the sides and bottom by imparting an appropriate gyratory motion with the arm during the cooling process. Separation of the mass from the crucible is usually easy, especially if aided by gentle pressure, and much less time is required for its disintegration than when allowed to solidify as a thick cake. If time is no object it is perhaps better to avoid all risk of deforming the crucible and proceed as follows: Let the melt solidify at the bottom of the crucible, first placing in it the bent end of a stout platinum wire. When all is solid, apply the flame again to melt only a thin layer next the crucible, when the cake can be lifted out with ease except for the little that still adheres to the vessel.

The contents of the crucible are placed in a rather tall covered beaker with some water, and hydrochloric acid of 1.1 specific gravity is added gradually in excess. The depth of the evanescent pink color usually produced on addition of the acid allows of judging approximately the amount of manganese present. The beaker is placed on the water bath, and when disintegration is complete, having been assisted by gentle pressure with a blunt glass rod, the contents are transferred to a large platinum dish and evaporated on the bath. It is permissible to dispense with the beaker and to perform the whole operation of solution in the platinum dish, but there will be greater solution of platinum in this case by reason of the action of the hydrochloric acid on sodium manganate, etc., in direct contact with platinum.

B. SUBSEQUENT TREATMENT.

From this point the treatment will be the same ordinarily whether the boric-oxide or the sodium-carbonate method of decomposition has been employed.

A. SEPARATION OF SILICA.

a. Reasons for adoption of accepted procedure.—The once universal practice of employing a single evaporation with hydrochloric acid for the dehydration of silica has been thoroughly discredited

by the work of a number of writers. R. Bunsen¹ was aware of the impossibility of separating silica by a single evaporation, and he corrected the alumina in his silicate analyses for the silica it was always found to contain. Later E. Ludwig² and still later C. Meineke³ drew renewed attention to the fact and insisted on the importance of correcting the alumina in the manner indicated. Ludwig and, at first, Meineke contented themselves with a single evaporation, and maintained that all of the unprecipitated silica was to be found with the subsequently precipitated iron and alumina. In his second paper Meineke prescribes two evaporations (presumably with intervening filtration) and the rejection of the silica subsequently recovered from the alumina as due to impurity in the ammonia or derived from the vessels, unless these were of platinum. He furnishes quantitative data.

In spite of these publications the practice continued of employing but a single evaporation. Some years later Alexander Cameron,⁴ seemingly in ignorance of the earlier work, reopened the subject with additional quantitative data, and insisted on more than one evaporation with intervening filtration instead of trying to recover the remaining silica from the alumina. He also showed, as Ludwig had asserted, that a common practice of evaporating to dryness several times with fresh portions of acid without intervening filtrations did not reduce the silica in the filtrate, and that the presence of aluminum, iron, and calcium was without influence on the results; further, that the dehydration was more complete when a high temperature was employed, but that it could not be made complete at one treatment by any modification of the process.

According to J. P. Gilbert,⁵ a drying temperature above that of the steam bath offers no advantage unless much magnesium is present, when the most favorable temperature is 120°. He found that much calcium chloride seems to facilitate dehydration of the silica, but that magnesium chloride above 120° by decomposing forms a silicate which dissolves in hydrochloric acid and increases the amount of silica carried into the filtrate. He confirmed the earlier belief that drying temperatures higher than that of the steam bath increase the amount of insoluble impurity in the silica, and that this amount can not be overcome by long digestion with hydrochloric acid. Further, he confirmed D. Lindo's statement⁶ that evaporation with sulphuric acid till the appearance of white fumes gives a higher result

¹ Ann. Chem. Pharm., vol. 61, 1847, p. 265.

² Zeitschr. anal. Chemie, vol. 9, 1870, p. 321.

³ Repert. anal. Chemie, vol. 7, 1887, pp. 215, 757.

⁴ Chem. News, vol. 69, 1894, p. 171.

⁵ Tech. Quart., vol. 3, 1890, p. 61; abstract in Zeitschr. anal. Chemie, vol. 29, 1890, p. 688.

⁶ Chem. News, vol. 60, 1889, p. 14.

in silica than with hydrochloric acid. But for general rock analysis the use of sulphuric acid at this stage must be rejected utterly.

Some of the above experiments of Cameron and Gilbert were repeated and confirmed by me.¹ In the course of this work it was found that hydrochloric acid itself exerts a marked solvent action on silica that has been separated from solution in any of the ways above outlined, whence it becomes plain how a portion of the silica always found in the filtrates gets there, and that it is hopeless to expect to prevent this by a single prolonged drying.² Other explanations commonly offered for the observed solubility are the formation of soluble silicates by interaction between the silica and salts present during drying and the protective influence of those salts. The former of these should become more active with increasing temperature, though Gilbert's work does not seem to indicate this except when magnesium is present in quantity.

A. B. Trickett³ and Lenher and Truog⁴ have shown that the sodium chloride always present after acidifying a solution of a sodium carbonate melt has a solvent action on silica. F. G. Hawley⁵ and H. A. B. Motherwell⁶ add confirmation, and Motherwell shows that other salts exert solvent action. Hawley found that concentrated hydrochloric acid is less active than that of 18 to 25 per cent strength, and, further, that, as was to be expected, the amount of silica dissolved is proportional to the amount of acid used.

C. Friedheim and A. Pinagel⁷ prescribe washing the silica with dilute hydrochloric acid instead of hot water because of the marked solubility in water observed by them. But, according to experiments made by myself to test this point, the direction is a vain one, for the results obtained by following it in the ordinary course of rock analysis were worse, if anything, than when pure water was used.

β. *Procedure in absence of notable amounts of fluorine.*—From the above observations the following procedure is deemed best adapted for general rock analysis in the absence of more than 0.2 or 0.3 per cent of fluorine.

The evaporating dish should be of platinum and as large as possible to permit considerable surface distribution of the dry mass. The dishes used in the Survey have a capacity of about 1 liter.

¹ Common errors in the determination of silica: Jour. Am. Chem. Soc. vol. 24, 1902, p. 262; Chem. News, vol. 86, 1902, pp. 79, 89. For details of experiments referred to here and on several of the following pages the reader will do well to refer to this paper.

² Max Wunder and A. Suleiman (Ann. chim. anal., vol. 19, 1914, p. 45) and V. Lenher and E. Truog (Jour. Am. Chem. Soc., vol. 38, 1916, p. 1050) confirm this statement. The former give quantitative data for the solubility of silica in hydrochloric, nitric, and sulphuric acids, and the latter for hydrochloric and sulphuric acids.

³ Mellor, J. F., Quantitative inorganic analysis, p. 175.

⁴ Jour. Am. Chem. Soc., vol. 38, 1916, p. 1050.

⁵ Eng. and Min. Jour., vol. 103, 1917, p. 541.

⁶ Idem, p. 1155.

⁷ Zeitschr. anorg. Chemie, vol. 45, 1905, p. 411.

Porcelain may be used, but never glass, if platinum is not available. Water or steam bath temperature suffices—is, indeed, demanded—for the evaporation to approximate dryness. If the analysis is begun in the morning the first filtration can be made late in the afternoon. Nothing is gained by continuing the evaporation long beyond apparent dryness this first time, for the slight reduction in the soluble silica gained by so doing is offset by a large loss of time; nor is there much advantage in crushing the residue to powder, whereby, moreover, the dish is easily scratched. The amount of silica passing into the filtrate will generally vary from 1 to 3 per cent of the amount present, and is but little less after 20 hours drying than after one-tenth of that time.¹ Upon the seemingly dry mass is poured enough strong hydrochloric acid to drench it thoroughly,² then an equal bulk of water, and the dish is placed covered on the bath for 10 to 30 minutes and the contents are stirred occasionally. It is quite permissible and sometimes advisable to defer adding the water till the strong acid has been in contact with the salts for 10 or 15 minutes. More water is then added and filtration proceeded with, first by decantation, leaving nearly all the silica in the bottom of the dish. The silica is generally in a coarse condition, and may be ground finer with a pestle. If there is a good deal of iron in the rock, it may be advisable at this stage to add hydrochloric acid of half strength and heat, after which the silica is brought onto the filter. It is not necessary to remove at this time the film of silica that may adhere to the dish in spots beyond the power of a stiff feather to remove, for in the subsequent evaporation it will disappear.³ The washing should be done with cold water or with hot dilute acid till the absence of any yellow color in the precipitate or paper indicates removal of most of the iron. Hot water may be used with advantage for the last washings, and the paper should be sucked dry at the pump.

The filtrate is evaporated again in the same dish to dryness. Usually this state will be reached by the following morning. It may be hastened, if desired, by placing the dish in an air bath at 110° or 120°. It is probable that a much higher temperature would have no bad effect in the majority of cases except to increase the amount of insoluble matter other than silica. If the data of experiments 6 to 9

¹ See Jour. Am. Chem. Soc., vol. 24, 1902, p. 366; Chem. News, vol. 86, 1902, p. 80.

² E. Jordis and W. Ludewig (Zeitschr. anorg. Chemie, vol. 47, 1905, p. 180) warn against loss by incautious moistening of the dry powder with water or acid, especially when these are hot, due to the throwing off of a cloud of dustlike particles. They recommend covering the dish and moistening cautiously with water before adding the acid. With a very capacious dish this is hardly called for.

³ Where but a single evaporation is contemplated this film may be removed by warming with ammonia and recovered by reevaporation with acid after driving off the ammonia. (See Kortright, F. L., Chem. Engineer, vol. 5, 1905, p. 19, who gives data to show the very material error that often results from neglect to recover this silica.)

in the paper already cited¹ are conclusive, they show that at this stage thorough drying exercises an appreciable effect in reducing the silica in the next filtrate, though the small amounts there reported when experimenting with pure quartz are not to be expected in rock work. If time is no object, and great accuracy is sought, a third evaporation and filtration should be made, for the silica in the second filtrate will amount to 2 to 4 mg.² Nearly the whole of this can be recovered later from the alumina, but not all, hence the advisability of securing as complete separation here as possible. The second and, if need be, third filtrations with their attendant operations consume less time than the first, and, of course, smaller filter papers are to be used. It is to be noted that these later silicas are more colored than the first, and if the rock is even moderately titaniferous they are by no means pure silica.³

Lenher and Truog in their paper already cited base the following procedure on their experimental work:

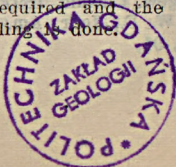
The cold fusion is treated with 60 cm.³ of hydrochloric acid (sp. g. 1.07). After all carbonates are decomposed and the lumps are broken up, evaporation on a steam or water bath is proceeded with until the residue begins to powder or crumble. Further evaporation should be avoided. Breaking up of lumps or crusts greatly expedites the evaporation near the end. The residue is treated with 15 cm.³ of hydrochloric acid (sp. g. 1.1), covered, and heated on the water bath for 10 minutes. After diluting with 10 cm.³ of water, filtration is proceeded with immediately, and the silica is washed with a hot solution consisting of 5 cm.³ of hydrochloric acid (sp. g. 1.2) to 95 cm.³ of water. This filtration is preferably performed with suction. The filtrate is evaporated to dryness and until the smell of acid has practically disappeared. The residue is dehydrated at 110° for two hours, taken up with 8 cm.³ of hydrochloric acid (sp. g. 1.1), covered, and heated on the water bath five to ten minutes, diluted to about 50 cm.³, and filtered immediately. This filtration is performed without suction, and the washing is done with cold water containing 1 cm.³ of concentrated hydrochloric acid to 99 of water.

By this procedure Lenher and Truog found the recovery of silica on a third evaporation not in excess of 0.3 mg. if a platinum dish was used, but more if the dish was of porcelain. The inference is that the glaze was attacked.

¹ Jour. Am. Chem. Soc., vol. 24, 1902, p. 306; Chem. News, vol. 86, 1902, pp. 79, 89.

² Lenher and Truog's more favorable results, Jour. Am. Chem. Soc., vol. 33, 1916, p. 1050, are not based on positive proof but merely on what they obtained by evaporation. They may have overlooked the possibility of a normal solubility of silica in the solution—silica which is not recoverable by evaporating to dryness.

³ Without giving quantitative data, A. LeClère (Compt. Rend., vol. 137, 1903, p. 50) claims that silica and titanium dioxide are rendered completely insoluble by acidifying the aqueous solution of the sodium carbonate melt with enough formic acid to give 5 per cent of free acid and keeping at a temperature of 100° for two days. As to titanium dioxide this claim has been verified at the Bureau of Standards by G. E. F. Lundell only if the solution is boiled during the two days, but not even so as to silica, very much of which remains in solution. The method need not be considered for rock analysis, both on account of the time required and the introduction of foreign matter from the glass vessel in which the boiling is done.



With minerals like the zeolites, or artificial products such as Portland cements, which are directly soluble in hydrochloric acid, the drying may be very much hastened by placing the covered dish, after bringing to approximate dryness on the bath, on a sand bath or on a triangle which itself rests on a hot plate. The temperature may rise in the dish to 200° ; in fact, according to Bertram Blount¹ it should not be lower. After an hour's exposure to this temperature less silica will perhaps pass into the filtrate than after prolonged drying at steam-bath temperature, but this is usually at the expense of greater contamination of the filtered silica. As this contamination is very large (see e, p. 104) with highly titaniferous and ferruginous rocks and minerals, the operator should use discretion in his choice of a high drying temperature.

γ. Procedure with rocks and minerals containing fluorine.—This subject has been touched on in commenting on the boric-oxide and sodium-carbonate methods of fusion,² and will be considered in detail under the heading "Fluorine" (p. 222).

b. IGNITION OF SILICA.

The application of a strong blast heat or its equivalent³ for 20 to 30 minutes with crucible covered is absolutely necessary to expel all moisture from the silica, and the latter is then not hygroscopic. The first of these statements, long extant in the literature, has been disputed by G. Lunge and C. Millberg⁴ on the basis of experiments made on silica obtained by the decomposition of silicon tetrafluoride by water. It has been shown,⁵ however, that while the objection holds good for silica thus prepared, it does not for silica obtained by the decomposition of an alkali silicate by means of an acid. F. P. Treadwell confirmed the observation as to the difference in behavior of the

¹ Jour. Soc. Chem. Ind., vol. 21, 1902, p. 1217.

² See A. a, p. 89, and footnote, p. 93.

³ It must be borne in mind that some platinum crucibles lose weight steadily and very appreciably on long blasting, not only when new but even after long use. When a crucible suffers from this defect the rate of loss should be ascertained from time to time and allowance made accordingly, or else the weight of the crucible should be taken after and not before ignition of the precipitate. (See on this subject Hall, E. W., Jour. Am. Chem. Soc., vol. 22, 1900, p. 494, and Hulett, G. A., and Berger, C. W., Jour. Am. Chem. Soc., vol. 26, 1904, p. 1512.) It was hoped that with the advent of the electric furnace prolonged ignitions would not be subject to this source of error, but it was soon found that at $1,250^{\circ}$, the maximum temperature attainable in the furnace at the Survey, medium-sized crucibles lost approximately 1 mg. in weight per hour. Similar losses have since been noticed and published by others. Their cause seems to be chiefly the distillation of iridium out of the alloy. At one time an error of about the same magnitude in the opposite direction caused perplexity until it was found that the platinum wire in the bedplate of the furnace was burned out. The crucible, then occupying the coolest place in the furnace, received a deposit of some of the metal volatilizing from the wires in the side plates. Iron has also been found repeatedly in platinum ware in large amount. (See p. 43.)

⁴ Zeitschr. angew. Chemie, 1897, p. 425.

⁵ Hillebrand, W. F., Jour. Am. Chem. Soc., vol. 24, 1902, pp. 372-373; Chem. News, vol. 86, 1902, p. 91.

two forms of silica, but regarded the blast as unnecessary if a Teclu instead of a Bunsen burner is used. Lenher and Truog say also that pure silica comes quickly to constant weight after ignition over a Meker burner. My experience is not in agreement with theirs.¹

Although with a powerful blast the above time limit usually suffices, and may be shortened materially for small amounts of silica, such as are usually found in limestones and even in cements, there is need occasionally to prolong it in very exact work until repeated weighings give the same value or a loss no greater than that suffered by the crucible itself.²

C. CORRECTION FOR IMPURITIES IN THE SILICA.

The weight of the crude silica should always be corrected for impurities, which are never entirely absent, by evaporating with sulphuric and hydrofluoric acids, which should be free from nonvolatile impurities, and again blasting for a minute or less, according to the amount of residue. It is a mistake to neglect another weighing at this point, even if the residue may appear insignificant. In my experience it has never been found to be unweighable, and, furthermore, the error due to loss in weight of the crucible itself is eliminated if the weighing is made. The silica in the crucible should be moistened with water before adding the hydrofluoric acid, though with strongly blasted silica the action is not so violent as with that which has not been thus treated. With rocks carrying 60 to 80 per cent of silica one or two drops of sulphuric acid diluted one-half suffice, but with less siliceous rocks the amount ought to be increased, not only in order surely to afford acid enough for the conversion of

¹ It was thought that the observation reported by E. Jordis and E. H. Kanter (*Zeitschr. anorg. Chemie*, vol. 35, 1903, p. 16), to the effect that artificially prepared silica when digested with hydrochloric acid takes up chlorine and holds it in a chemical combination that is only incompletely broken up on ignition, might have bearing on this point. To test this, precipitated silica was fused with sodium carbonate, the melt was dissolved in water and evaporated with hydrochloric acid as in silicate analysis, and the separated silica was washed with cold water till free from all but a hardly detectable trace of chlorine (wash-water test) and dried at gentle heat. Instead of the large amount of chlorine reported by Jordis and Kanter, this silica yielded only the minute trace that blank tests with the reagents afforded, and sodium in weighable amount was also absent. Evidently, as stated by Jordis and Kanter, the chlorine compound, if it exists, is readily decomposed by water. The tests for chlorine were made by dissolving the silica in presence of silver nitrate in hydrofluoric acid free from chlorine, also by fusing with chlorine-free sodium carbonate, dissolving in water, acidifying with nitric acid, and then adding silver nitrate. Th. Bauer (*Thonind. Ztg.*, vol. 37, 1913, p. 89) believes also that incompletely washed silica contains an oxychloride of silicon, soluble in water but not readily decomposed by ignition. If he prepared his silica from alkali melts it may have held sodium chloride.

² For the proof see Hillebrand, W. F., *Jour. Am. Chem. Soc.*, vol. 24, 1902, p. 373; *Chem. News*, vol. 86, 1902, p. 91. The duty of every analyst to test the efficiency of his blast or muffle can not be emphasized too strongly. The discordance of many statements and results on a variety of subjects is to be attributed to a difference in the ignition temperature employed by different writers. A really good blast will readily melt a few centigrams of orthoclase powder in the bottom of a 15-gram platinum crucible, showing a temperature of probably 1,200°.

all the contaminating bases to sulphate, but also to prevent loss of titanium by volatilization as fluoride, for with increasingly basic character of the rocks the percentage of this element in the residue is likely to increase.

Precipitated silica is easily removed by one evaporation with a sufficiency of hydrofluoric acid, but if quartz happens to be present this is not the case, for it is dissolved but slowly, and more than one treatment may be necessary.

The subsequent precipitate of alumina, etc., is usually ignited in the crucible containing the residue from the silica.

d. ACCURACY OF THE SILICA DETERMINATION.

By observing the above rules—use of platinum, repeated evaporations and filtrations, proper blast ignition, and correction for foreign matter—the determination of silica, from being one subject to grave error, has become one of the most exact of which I have cognizance, provided precautions are taken to recover, as hereinafter described, the portions that are to be found inevitably with the alumina. With careful work variations of 0.1 per cent are the exception in duplicate analyses.

e. COMPOSITION OF THE RESIDUE OBTAINED FROM THE SILICA.

The qualitative composition of the residue obtained from the silica varies with different rocks less than its quantity. The residue will contain alumina and ferric, titanic, and phosphoric oxides invariably if these are present in the rock. If the rock is low in the last three, particularly the last two, the residue should be slight, occasionally less than 1 mg. Usually it is much greater, and it may amount to 2 or even 3 per cent with basic rocks very rich in titanium and phosphorus. It is, however, a great mistake to suppose, as some chemists still seem to, that all or nearly all the titanium is to be found with the silica. It may reach one-third of the total amount.

If in correcting the silica, toward the end of the evaporation, when the hydrofluoric acid has been driven off and the sulphates begin to appear in solid form, the residue has a peculiar milky or enamel-like appearance, it may be taken as evidence of much phosphorus and titanium, though possibly the appearance may be due to zirconium with the other elements named. Although observed in but one series of rocks,¹ the appearance is so unusual and striking that it was deemed worthy of record.

It might be supposed that the residue would contain most of the barium of those rocks carrying that element together with sulphur or sulphates, but in my experience this is not so. Only when there is considerable excess of SO_3 over BaO will any of the latter be present

¹ See first footnote, p. 119.

in the residue, and in the vast majority of cases there is none at all. This is due to the appreciable solubility of barium sulphate in hot hydrochloric acid, coupled with the fact that barium is so minor a constituent of most rocks. Should some of it be present in the residue, its removal and estimation at this stage are not necessary, as it can be recovered more conveniently later, together with the silica accompanying the precipitate of alumina, etc. (9. B. b, p. 118).

Quite as rarely is calcium ever a component of the residue if the decomposition of the rock powder was complete at the outset. I have found frequently that the residue, after re-solution, is quantitatively precipitable by ammonia in presence of an ammonium salt. W. R. Bloor,¹ however, in analyzing clays, invariably found calcium and magnesium as well as alkalis in this residue in amounts that were surprisingly large, considering the relatively small percentages of these elements in clays. I have since tested the matter carefully as to calcium and magnesium, finding none of the former and but 0.2 to 0.3 mg. of MgO, when present at all.

F. A. Gooch, F. C. Reckert, and S. B. Kuzirian² and later Kuzirian³ assume without proof that sodium chloride is one cause of persistent loss of weight when silica is ignited. My own observations, like later ones of Lenher and Truog,⁴ are quite opposed to this.

F. PLATINUM IN FILTRATES.

The filtrates from the silica always contain notable amounts of platinum. This arises in very small degree from the crucible fusion, unless niter was added; in a larger degree indirectly from the action of hydrochloric acid on the manganate, vanadate, and sometimes chromate of sodium; and, if much iron is present, in no small degree from the reduction of ferric chloride to ferrous by the platinum of the dish. This last reaction has attracted little attention until recently, but it is mentioned by Gmelin-Kraut⁵ and can be demonstrated readily by evaporation of ferric chloride in platinum.

The removal of this platinum before precipitating alumina and iron is not necessary (but see footnote, p. 119) and to do so involves the reoxidation of all iron and subsequent boiling to remove or destroy the excess of oxidizing agent, together with the expenditure of much valuable time. The iron is already oxidized by the fusion, and needs no further help in that direction. In the following descriptions it is assumed that the platinum has not been eliminated at this stage.

¹ Jour. Am. Chem. Soc., vol. 29, 1907, p. 1603.

² Am. Jour. Sci., 4th ser., vol. 36, 1914, p. 598; Chem. News, vol. 110, 1914, p. 202; Zeitschr. anorg. Chemie, vol. 85, 1914, p. 430.

³ Am. Jour. Sci., 4th ser., vol. 37, 1914, p. 61; Chem. News, vol. 109, 1914, p. 184; Zeitschr. anorg. Chemie, vol. 85, 1914, p. 430.

⁴ Jour. Am. Chem. Soc., vol. 38, 1916, p. 1050.

⁵ Anorganische Chemie, 6th rev. ed., vol. 3, 1875, p. 359.

7. METALS PRECIPITABLE BY HYDROGEN SULPHIDE.

The presence in appreciable amounts of metals precipitable by hydrogen sulphide, except perhaps copper, is of so infrequent occurrence in most rocks that discussion is unnecessary in their connection. In case it is necessary to precipitate them at this stage, however, it is always well to bear in mind that a little titanium may be thrown down along with them. Separations of the silica should be made in porcelain, to eliminate platinum; or, better still, the quantitative determination of these metals should be made in a separate portion of the rock broken up by the action of hydrofluoric and sulphuric acids.

The warning may here be repeated that the samples should never be passed through copper or brass sieves when copper or copper and zinc are sought.

8. JOINT PRECIPITATION OF ALUMINUM, IRON, TITANIUM, ZIRCONIUM, CHROMIUM, RARE EARTHS, PHOSPHORUS, AND VANADIUM, WITH AND WITHOUT MANGANESE.

A. PRELIMINARY REMARKS.

The difficulties are very great in the way of successfully producing and handling the complex precipitate which is obtained in the next stage of the analysis and which should contain the aluminum, iron, titanium, and phosphorus, besides chromium, vanadium, zirconium, and rare earths if present, and according to some preferences the manganese. It is recognized fully that there are objections to parts of the procedure that has been followed in the Survey laboratory, but the same may be said of any other that is known. It is believed that the Survey procedure, which in its main features is closely modeled after old and well-known methods, will give in competent hands quite as satisfactory if not better results than any other.

B. PRECIPITATION WITHOUT MANGANESE.

a. PRECIPITATION BY AMMONIA.

α. Preliminary remarks.—Two precipitations by ammonia at boiling heat are usually quite sufficient to separate iron, aluminum,¹ phosphorus, vanadium, chromium, titanium, rare earths, and zirconium, if all these are present, from nickel, manganese, the alkaline-earth metals, and magnesium, in the relative proportions in which these elements ordinarily occur in rocks, provided ammoniacal salts are present in sufficient quantity. This last point is of special im-

¹ It is well to bear in mind that in presence of fluorine, aluminum is precipitated very incompletely by ammonia. See footnote, p. 90.

portance as regards magnesium, and failure to observe it is doubtless the reason why many old analyses, and sometimes modern ones, show utterly improbable percentages of alumina, especially as chemists were formerly often satisfied with a single precipitation. The necessary ammonium chloride is obtained better by the use of purified ammonia water and hydrochloric acid than by the addition of the solid salt, which is seldom pure. The chemist should satisfy himself what amounts of ammonium salt are needed to hold in ammoniacal solution the maximum percentage of magnesium that the rock he is analyzing might contain. With extremely high magnesian rocks a third precipitation is generally requisite, and a minute amount of calcium will sometimes be found in the third filtrate, unless the procedure given under β is followed carefully.

The precipitations are made in a bulk of 300 to 400 cm.³, at boiling heat, in a platinum dish if possible, otherwise in one of the borosilicate beakers of the "pyrex" type (free from zinc). The ammonia should be as free from carbonate as possible, as well as from any nonvolatile matter.

Very many inconclusive researches have been conducted to determine the best conditions for the precipitation of aluminum as the hydroxide. Some writers have regarded even a slight excess of ammonia as objectionable; others not. The failure to come to agreement seems to be due to the fact that the hydroxide has a certain solubility in ammonia and that the hydroxyl concentration at which this solubility is least was unknown. Recent work of W. Blum¹ at the Bureau of Standards has settled the latter point in favor of the concentration which is indicated by the change of color of methyl red or rosolic acid in acid solution—that is, $[H]^+ = 10^{-7}$ (about). Methyl red is preferred because of its sharper color change. Blum's recommendations for precipitation are the following:

β . *Procedure*.—To the solution containing at least 5 grams of ammonium chloride per 200 cm.³ of solution, or an equivalent amount of hydrochloric acid, add a few drops of methyl red (0.2 per cent alcoholic solution) and heat just to boiling. Carefully add dilute ammonium hydroxide drop by drop until the color of the solution changes to a distinct yellow. Boil the solution for one to two minutes and filter at once. Wash the precipitate thoroughly with hot ammonium chloride or nitrate solution (2 per cent).

The correct end point would be difficult to determine in presence of much iron were it not for the fact that ferric iron precipitates before the solution is alkaline to methyl red; hence it is easy to obtain the correct end point by adding at first only enough ammonia to precipitate the iron upon short boiling and allowing the ferric

¹ Sci. Paper Bur. Standards No. 236, 1916; Jour. Am. Chem. Soc., vol. 38, 1916, p. 1282.

hydroxide to settle, after which the color of the indicator can be recognized readily in the supernatant liquid and more ammonia added if necessary, or any large excess may be neutralized with dilute acid.

Blum found that, after a single precipitation, separation from calcium and barium is perfect, and from magnesium nearly so; and that aluminum itself was so completely precipitated that a maximum of only 0.3 mg. Al_2O_3 could be found in the combined filtrates and washings.

As to the behavior of manganese, G. E. F. Lundell and H. B. Knowles, of the Bureau of Standards, found that after two precipitations less than 0.1 mg. of it, calculated as Mn_3O_4 , had been carried down when there was present originally 10 mg. of MnO , and less than 1 mg. with 200 mg. MnO originally present. The separation seems therefore to be practically perfect for rock analysis.

Further experiments by Lundell as to the behavior of vanadium seemed to show that in rock analysis practically all the vanadium will be in the precipitate when R_2O_3 is high, with Fe_2O_3 preponderating and V_2O_5 low, a point which is of importance in the subsequent determination of the iron. When Al_2O_3 preponderates the precipitation of vanadium is less complete. Vanadium in the quadrivalent state is more completely precipitated than vanadium in the quinquevalent state. It is probable that the evaporation with hydrochloric acid to dehydrate silica reduces the vanadium to the former state. These observations bear out a statement made by F. J. Pope¹ that vanadium can not be precipitated completely with aluminum by ammonia, but that it is precipitated with iron and titanium when in the quinquevalent state provided that no excess of ammonia is present.

The use of a dilute solution of an ammonium salt as a wash liquid instead of water is necessary in order to avoid as much as possible resolution of some of the aluminum hydroxide. S. L. Penfield and D. N. Harper² recommend washing with a dilute solution of ammonium nitrate (20 cm.³ nitric acid neutralized with ammonia to the liter), and also the solution of the first precipitate in nitric instead of hydrochloric acid in order to shorten the washing, there being no chloride to remove.³

¹ Trans. Am. Inst. Min. Eng., vol. 29, 1899, p. 372.

² Am. Jour. Sci., 3d ser., vol. 32, 1886, p. 112. C. F. Sidener and E. Pettijohn's statement (Jour. Ind. Eng. Chemistry, vol. 8, 1916, p. 714) that ammonium nitrate exerts about as much solvent effect as pure water on aluminum hydroxide is opposed to that of Penfield and Harper and to the experience of Blum (op. cit.).

³ A single objection, and that of a practical nature, weighs against these suggestions. It will not do to evaporate to dryness filtrates containing both chlorides and nitrates in the same platinum dish, still less to drive off the mixed ammoniacal salts in platinum. Contrary to numerous earlier statements there is no danger of loss of aluminum chloride by volatilization when the precipitate is ignited before complete removal of ammonium chloride, an assertion which has been confirmed by more than one recent writer. Iron also is not volatilized by ignition in presence of as much as 1 per cent of ammonium chloride (Daudt, H. W., Jour. Ind. Eng. Chemistry, vol. 7, 1915, p. 847).

For a reason mentioned under E (p. 114) the final precipitation may be made with advantage in the presence of macerated filter paper, as recommended by Dittrich,¹ and the precipitate should be sucked dry.

In the presence of little or no manganese, and also in the absence of iron, the ammonia method of precipitation is preferable by far to the basic-acetate method described in the following section, but it will occasionally happen that the separation from even very small amounts of manganese is altogether incomplete, and the uncertainty of insuring this separation led me to employ the basic-acetate method for the first precipitation in all cases where manganese is present—and the exceptions are few—even though the precipitation of alumina is sometimes less complete than by ammonia, and in spite of other admitted defects, as, for instance, a tendency of the precipitate to run through the filter on washing.²

The most likely explanation of the persistent retention of small amounts of manganese by the precipitates produced by ammonia or acetates, even after repeated precipitation, seems to be that a portion of the manganese becomes oxidized to the Mn_2O_3 state and remains so when redissolved, being then in a fit condition for reprecipitation.

D. THE BASIC-ACETATE PRECIPITATION.

a. Preliminary remarks.—Although for the basic-acetate precipitation most writers seem to prescribe or prefer sodium acetate, except when the presence of a fixed alkali would interfere with subsequent operations, there does not seem to be any valid reason why ammonium acetate should not do quite as good service, besides having the advantage of easy removability afterward in case of need. Also, there is probably no good reason why the corresponding carbonates instead of the hydroxides should be used for neutralizing the hydrochloric solution before adding the acetate other than the fact that they were, when the methods originated, and still are easier to obtain comparatively free from silica and alumina. It is to be borne in mind that with precipitates low in iron and high in aluminum the separations are less satisfactory than when the reverse condition prevails. In rocks alumina usually predominates, often largely, over iron oxide, so

¹ Anleitung zur Gesteinsanalyse, 1905, pp. 10, 11, 14; Ber. Deutsch. chem. Gesell., vol. 37, 1904, p. 1840.

² The fact must not be overlooked that certain of the rare earths may pass completely into the filtrate if the basic-acetate method is followed. If, then, later, on rendering the combined filtrates ammoniacal, an unexpectedly large precipitate appears, this should be examined carefully as to its nature. In an analysis of piedmontite from Maryland over 2 per cent of rare earths, including cerium and others not identified were quantitatively separated in this way from iron, alumina, etc. On the other hand F. J. Pope (Trans. Am. Inst. Min. Eng., vol. 29, 1899, p. 372) says that quinquivalent vanadium is completely precipitated, which is a very desirable effect.

that none of the methods of making the basic-acetate separation that involve the presence of notable quantities of free acetic acid are permissible, because of the solubility of aluminum hydroxide in this acid even when it is very dilute.

β. Procedure.—The cold and not excessively acid solution, not exceeding 100 cm.³ in bulk and contained in a beaker of resistant glass, is first neutralized with great care by adding a freshly prepared solution of sodium carbonate drop by drop. When the solution begins to deepen in color, the addition of the carbonate is continued with less speed and with longer stirring between the successive drops. When, now, the precipitate that each drop causes begins to dissolve very slowly, no further addition may be made till the liquid becomes quite clear again. With practice, it is not difficult to recognize this condition, even when the liquid is very dark. The intensity of the color will depend on the amount of iron present and the degree of dilution; therefore with small amounts of iron one is much more liable to overstep the end point than with solutions rich in iron. When, in spite of vigorous stirring, the turbidity after a final drop seems rather to increase than diminish, one or, if need be, two drops of acid are added. If this does not clear the liquid, it is best to add a slight excess and to repeat the neutralizing process.

Two or three grams of sodium acetate dissolved in a small amount of water are now poured in and then boiling water till the total bulk is about 400 cm.³ The beaker is placed over a lamp and its contents are brought to boiling and kept in that state for two or three minutes. As soon as settling has taken place filtration is proceeded with. It is generally best to dispense with the pump at this stage and to use a filter of such size that the whole of the precipitate can be brought upon it conveniently without filling to the top. The washing is to be done with hot water, to which has been added a very little sodium acetate for the purpose of guarding against an otherwise inevitable turbid filtrate.

The precipitate, having been sucked dry at the pump, is redissolved in hydrochloric acid, reprecipitated by ammonia as in B. *β* (p. 107), washed, sucked dry, and treated as in E (p. 114), after recovery as in D. b (p. 113) of the portions of aluminum and iron that may have passed into the filtrates.¹

¹ Modifications of the basic acetate separation. *Borck's method.*—H. Borck (Zeitschr. angew. Chemie, vol. 25, 1912, p. 719) makes the basic acetate precipitation by adding ammonia in presence of methyl orange until the color changes, then ammonium acetate, and finally boiling for a short time.

Sánchez's method.—J. A. Sánchez (Bull. Soc. chim., vol. 9, 1912, p. 880) separates ferric iron from bivalent manganese in neutral or faintly acid solution by adding pyridine and then heating. The ferric hydroxide is washed with hot water holding pyridine and then with pure water. It is claimed that half a milligram of manganese can be separated thus from a gram of iron. If much manganese is present the precipitate is to be dissolved in hydrochloric acid and the separation repeated. Zinc accompanies the

C. PRECIPITATION TOGETHER WITH MANGANESE.

a. BY AMMONIA AND AMMONIUM PERSULPHATE.

α. Preliminary remarks.—This method has for its object the coprecipitation of manganese with a view to simplifying subsequent operations. It is, however, defective in case the rock carries appreciable amounts of barium and strontium or is very high in calcium, by reason of the certain partial precipitation of some of one or both of the first two as sulphates and its possibility in the case of calcium.

iron in part, but can be separated from it, after dissolving in hydrochloric acid, by ammonia in presence of ammonium chloride.

Mittasch's method.—A study of the conditions necessary for successful separations of large or small quantities of manganese from iron by one treatment has been made by A. Mittasch (*Zeitschr. anal. Chemie*, vol. 42, 1903, p. 492), who gives the following directions for the use of ammonium acetate. It must be borne in mind, however, that this method is not applicable to aluminous materials.

The solution containing not much free acid (hydrochloric) and preferably cool, whose volume should not exceed 100 cm.³, is neutralized in a beaker with concentrated ammonium-carbonate solution (200 grams per liter, about double molar) till the precipitate that is formed begins to redissolve slowly, then with weaker solution (about one-tenth molar) till a slight precipitate persists for one or two minutes in spite of stirring. Next is added, according to the amount of this precipitate, 3 to 5 cm.³ of acetic acid (double normal) if the commercial article of ammonium acetate, which nearly corresponds to the acid salt $(\text{NH}_4)\text{C}_2\text{H}_3\text{O}_2\cdot\text{C}_2\text{H}_3\text{O}_2$, is used, or 10 cm.³ if the normal salt is used. The last is made by neutralizing acetic acid with ammonia. The solution is then diluted with water to about 400 cm.³ and brought nearly to the boiling point. Any precipitate that may have appeared being disregarded, 20 cm.³ of the acid acetate (one-half molar) or 5 cm.³ of acetic acid and 10 cm.³ of the normal acetate (molar) is added, and the boiling temperature is maintained for a minute longer. Precipitation is complete even at 60°, but filtration is easier if the boiling temperature is reached. As soon as the solution is settled filtration is begun and the washing performed with hot water at first, then with hot water containing some acetate and a little acetic acid. Any adhering film is removed from the glass with hydrochloric acid and reprecipitated with ammonia. If this is added to the main filter it must not be done till the large precipitate has been washed completely, because of the danger of precipitating, by the ammonia, manganese that has not yet been washed out.

Brunck-Funk method.—The following method of O. Brunck (*Chem. Zeitung*, vol. 28, 1904, p. 514), slightly modified and extended by W. Funk (*Zeitschr. anal. Chemie*, vol. 45, 1906, p. 181), is claimed to afford a complete separation, by one treatment, of iron from manganese, zinc, nickel, and cobalt. Its applicability to aluminous materials, however, has not been tested, and it is quite improbable that it would work with rocks containing phosphorus and titanium.

The method differs from other modifications of the acetate process in the avoidance of the delicate neutralization, by removing excess of acid by evaporation, and in the addition of potassium chloride to form a double salt with ferric iron and thus prevent the separation of a basic chloride during the drying. As given by Funk for materials soluble in acids the procedure is as follows:

To the chloride solution in a large dish is added potassium chloride (about 0.35 gram to 0.1 gram of iron), and the solution is evaporated to apparent dryness on the steam bath but without expelling all of the free acid. The residue is broken up superficially, and the drying on the bath continued for 5 to 10 minutes. It is then taken up in 10 to 20 cm.³ of cold water, with which it should give a clear solution. It is requisite that there shall remain a slight amount of free acid to set free acetic acid from the acetate in the next stage of the operations. One and a half to two times the theoretically needed quantity of sodium acetate (3 molecules of $\text{NaC}_2\text{H}_3\text{O}_2\cdot 3\text{H}_2\text{O}$ to 1 atom of iron) is now added, in a solution which has been rendered slightly acid with acetic acid if originally alkaline. After diluting with cold water (to 400 to 500 cm.³ for 0.2 gram iron) the solution is gradually heated with stirring to the point of precipitation (60° to 70°), allowed to settle, and decanted, the precipitate being collected on the filter and washed with hot water.

It is probable that calcium can be completely held in the filtrates by two precipitations in analyzing almost any silicate rock, but this is not at all certain with respect to limestones, a point that has not yet been investigated. If neither strontium nor calcium is present in sufficient amount to be retained in the precipitate, there is no vital objection to the method on this score, for barium can be recovered, as in 9. B. b (p. 118).

The applicability of the method as above limited being assumed, it may be carried out as follows, though too few tests have thus far been made to warrant its unqualified recommendation.

β. *Procedure.*—To the filtrate from the silica contained in a platinum dish, and in bulk from 100 to 200 cm.³, is added enough hydrochloric acid to prevent precipitation of magnesium when made ammoniacal (see B. a. α, p. 106). Heat is applied, and about 1 gram of ammonium persulphate¹ free from all interfering impurities is added. When the liquid begins to boil ammonia is added carefully until in decided excess, as shown by the odor, and boiling is kept up for several minutes.² The precipitate is allowed to settle, is filtered quickly, washed three or four times with 2 per cent ammonium chloride solution, and sucked dry by the pump. It has not been determined if such a very dilute solution of persulphate has any appreciable effect on glass, but apparently not, to judge from my own limited experience. The precipitate is then dissolved in a small amount of hot hydrochloric acid containing a few drops of sulphurous acid, and after addition of well-macerated filter paper is reprecipitated precisely as the first time, washed three or four times with 2 per cent ammonium chloride solution, then ignited in the paper, and

¹ This reagent may have to be purified before use. Jannasch (*Praktische Leitfaden der Gewichtsanalyse*, 2d ed., 1904, p. 179) does this as follows: To a warm saturated solution (not over 95°) ammonia is added until its odor persists. [More will have to be added at intervals, for the continual decomposition of persulphate sets free sulphuric acid.—W. F. H.] When the precipitate of alumina, etc., has settled, the solution is filtered as rapidly as possible through asbestos, a porcelain funnel being used, because the strong solution attacks both paper and glass markedly. When cooled to about 30° the clear filtrate is poured into twice its volume of alcohol and further cooled by ice applied externally. After half an hour the precipitated persulphate is collected on a filter, washed with alcohol and then with ether, and dried in the air. The alcohol must be removed thoroughly.

A commercial article purified thus by me was found to contain no interfering impurities, though not free from alkali, and it held moreover much ammonium sulphate—nearly 50 per cent in one preparation.

The reagent as bought should be tested always as to strength as well as for alumina and other impurities. B. E. Sive, at the Bureau of Standards, recently found an article of domestic make, purchased in 1912 and labeled 97.9 per cent, to contain only 3.5 per cent of persulphate. Two other lots, one of domestic and one of foreign origin, purchased in the same year, held 95 and 99.25 per cent, respectively.

Because of the decomposition and consequent loss that results when Jannasch's method of purification is employed, H. E. Merwin has suggested (private communication) that, if aluminum is the only interfering element, its content be determined and a correction made for it, using of course a weighted amount of the reagent for the rock analysis.

² It has not been determined if Blum's manner of precipitating (8. B. β. p. 107) is permissible under the conditions here existing.

weighed as Al_2O_3 , Fe_2O_3 , Mn_3O_4 , TiO_2 , and P_2O_5 .¹ Any chromium in the rock should be in the filtrates, wholly oxidized by the persulphate, but it will be recovered with the unprecipitated traces of alumina, as detailed under D. c, page 114, and should be added to the main precipitate above. It is not best to attempt to determine the chromium colorimetrically in the filtrate.

b. BY AMMONIA AND AMMONIUM SULPHIDE.

Although the old method of precipitation by ammonia and ammonium sulphide can be employed in special cases, it is not well adapted generally to silicate rocks and therefore will not be described in this connection.

D. RECOVERY OF UNPRECIPITATED IRON AND ALUMINUM FROM THE FILTRATES.

a. AFTER AN AMMONIA PRECIPITATION.

The filtrates are evaporated to a small volume, always in platinum if possible and allowable. If ammonium salts are present in abundance it is advisable to evaporate the filtrates separately, the second to dryness. Its dry contents, almost wholly ammonium salt, are expelled by heat, the slight residue being taken up with hydrochloric acid and added, whether wholly soluble or not, to the other filtrate reduced in bulk. To this ammonia is now added and the evaporation continued, the solution being kept alkaline, in order to coagulate the small amount of alumina that will invariably and the iron hydroxide that will usually be found. This is collected on a small filter and the filtrate caught in a flask of 150 to 200 cm.³ capacity, if manganese is to be determined, otherwise in a platinum dish of suitable capacity for the calcium precipitation. The small precipitate is washed with 2 per cent ammonium chloride solution, burned, and added to the main one.

b. AFTER A BASIC-ACETATE PRECIPITATION.

The first filtrate is evaporated to or nearly to dryness, in order to get rid of the excess of acetic acid. The residue is then taken up with only enough hot water to keep it in solution, and the dish is replaced on the bath for a short time. The precipitate, which will generally be appreciably larger than that obtained in a, is collected on a small filter (7 cm.), and the filtrate in a flask of 150 to 200 cm.³ capacity. The second or ammoniacal filtrate, having been separately evaporated to small bulk, with the addition of a few drops of ammonia toward the end, serves as first wash water for the other dish and for the pre-

¹ The mixture will contain also ZrO_2 , V_2O_5 , and the rare earths, if present.

precipitate on the filter. Both dishes and the filter are finally rinsed with 2 per cent ammonium chloride solution. The ammoniacal filtrate contains enough ammonium salts to prevent precipitation of magnesium in the first filtrate when the two come together.

If manganese peroxide has been deposited on the surface of the dish it is removed by hydrochloric acid and a drop or two of sulphurous acid, which mixture is then passed hot through the filter, the filtrate being caught in a small beaker. A reprecipitation by ammonia is then made, and the precipitate collected again on the filter and added to the main one, the filtrate passing into the flask containing the previous filtrate. If much manganese is present, of course, a second precipitation by ammonia of the small precipitate may be required. In these cases there is no difficulty in getting all the manganese into the filtrate.

C. AFTER PRECIPITATION BY AMMONIA AND AMMONIUM PERSULPHATE.

The filtrates are evaporated as in a. The second filtrate is carried to dryness and the ammoniacal salts are removed by ignition. The residue is treated with a little hot hydrochloric acid and added to the first. A drop or two of sulphurous acid is then added if chromium is present, as will be shown usually by a yellowish color of the solution. The aluminum, chromium, and trace of iron are then precipitated by ammonia in slight excess and the digestion is allowed to proceed on the bath till the slight precipitate has coagulated. This is collected on a small filter (7 cm.) and washed with hot water, the filtrate being collected as in a and b if nickel or zinc are to be looked for, otherwise in a large platinum dish for treatment as in 12 (p. 140).

The precipitate is redissolved in hydrochloric acid, reprecipitated in small bulk of solution by ammonia, and finally added to the main precipitate obtained in C. a (p. 111).

E. IGNITION OF THE PRECIPITATE.

The combined precipitates of alumina, etc., obtained in either B, or C, and D, are ignited without preliminary drying in the crucible containing the residue from the silica (6. B. c, p. 103), unless considerable iron is present. In that case the main precipitate is dried and removed as far as possible from the paper, which is ignited separately to prevent partial reduction of a portion of the iron oxide. This is especially necessary when the precipitates were obtained without using macerated filter paper, in which case they are lumpy after ignition, and any magnetic oxide that may have been formed can not be reoxidized wholly by heating or by treatment with nitric acid. (See 5. A. c. β , p. 76.) They are also slow to yield to subsequent treatment. A precipitate formed in presence of thoroughly macerated

paper, as recommended by Dittrich, on the other hand, yields on ignition a powder, and the fine state of division makes reoxidation of any reduced iron easy, besides wonderfully shortening the time required for subsequent re-solution.

M. F. Connor,¹ instead of using macerated paper, moistens the washed and dried precipitate, separated from the paper, with an alcoholic solution of ammonium nitrate, dries again, and ignites. The paper is ignited separately.

Alumina in the quantities usually found can not be dehydrated completely by the full heat of the ordinary Bunsen burner.² It must be blasted for 5 or 10 minutes. If iron is present in large amount this blasting must be so conducted as to insure access of air to the crucible (6. A. d. γ , p. 95).

For ignitions of this kind, which involve no very prolonged heating, an electric furnace is well adapted by reason of its nonreducing atmosphere, provided the temperature is not high enough to cause by temperature alone reduction of ferric to magnetic oxide of iron.

The crucible itself may have changed in weight since the silica was ignited in it. Its correct weight is found after treatment of its contents as explained in the next section.

9. DETERMINATION OF THE OXIDES OF IRON AND SILICON IN THE PRECIPITATE OBTAINED UNDER 8.

A. PRELIMINARY REMARKS.

The common practice in the Survey laboratory has been to find alumina by difference after deducting from the precipitate produced by ammonia, sodium acetate, or ammonia and ammonium persulphate the sum of all other oxides this precipitate may contain. Of these only ferric oxide, titanite oxide, and the small amount of residual silica not recovered by the procedure detailed in section 6, and in rare instances perhaps a little barium, are determined in this portion. (See also footnote 2, p. 119, regarding possibly contaminating platinum.) The oxides of phosphorus, vanadium, chromium, rare earths, and sometimes manganese are looked for in other portions of the rock powder. Glucinum and uranium are not considered. This throws on the alumina all errors that are involved in their separate determination, but these may balance. In any event the probable error can hardly be as high as that involved in the direct determination of the alumina itself, considering the difficulty of effecting a satisfactory separation of it from the other components of the mixture, an operation which would, moreover, extend immoderately the time required for each analysis.

¹ Cong. géol. internat., 12^e sess. Canada, 1913, p. 885.

² A statement which perhaps originated with A. Mitscherlich (Zeitschr. anal. Chemie, vol. 1, 1862, p. 67) and has been confirmed by me and very many other authors.

Phosphorus can not be determined in the ignited oxides after these have been fused with pyrosulphate (B. a, below), for the reason that the treatment volatilizes some of it. Fuming of a phosphate with sulphuric acid also volatilizes P_2O_5 . H. Rose, in his "Hand-book of quantitative analysis," mentions this possibility, and the fact was long ago confirmed by me and again recently by careful tests, as yet unpublished, that were made at the Bureau of Standards. The loss may be large, depending upon the amount of sulphuric acid used and the rate at which it is driven off.

In section 10, below, are presented various procedures of separation differing from those which immediately follow here and which may be used under special conditions or by preference of the experienced analyst. In the main they are described only in so far as they have to do with the mixture of oxides treated of in section 8, the ultimate determination of the constituents of the fractions being described fully under the sections on titanium, zirconium, chromium, phosphorus, and vanadium.

The first step is to obtain the ignited oxides in a suitable solution. Some earlier writers recommended dissolving the oxides in hydrochloric acid, but this is a most ineffective mode of attack. Perfect solution is effected in the manner detailed in the next paragraph.

B. RESIDUAL SILICA (BARIUM).

a. SILICA.

The weighed precipitate is transferred as far as possible to another crucible of 25 to 30 grams weight.¹ The small adhering residue, chiefly that originally derived from the main silica, is brought into solution by fusion with a small amount of sodium or potassium pyrosulphate. This fusion takes but a few minutes, and must not be continued beyond the time actually needed, otherwise it will be impossible, after cleaning and igniting, to get the correct weight the crucible possessed after the ignition of the alumina.² The hot liquid is poured onto the main mass of precipitate in the other crucible, more pyrosulphate is added (up to 7 grams in all),³ and the fusion is renewed

¹ This crucible may be of gold, as that metal is less attacked by the subsequent treatment than platinum. If gold is used the remarks in the text concerning the recovery of dissolved platinum apply to the dissolved gold.

² It will be remembered (see p. 102, footnote 3) that long blasts or furnace ignition of the silica may have reduced the weight of the crucible by an appreciable amount, hence the need for getting its weight empty at this point.

³ The total weight of pyrosulphate used should be known approximately in order to correct later for its effect on the colorimetric determination of the titanium (p. 161).

A chief objection raised by many to the use of an alkali bisulphate for bringing this precipitate into solution is that so much care is needed during a fusion to prevent frothing and boiling over, which involves a very gradual application of the heat and consequent greater expenditure of time. The objection is sound as applied to the bisulphate, but is swept away if the latter is first converted into pyrosulphate, which is always its condition after the frothing has ceased. To effect this change it is only necessary to melt a

and continued until the whole has been dissolved, which in the case of the potassium salt is always easy to be seen, even when the liquid appears dark red and opaque, by removing the crucible from the flame to a good light and allowing to cool. At one point in the cooling the liquid becomes transparent and allows the bottom of the crucible to be seen. This is less the case with the sodium salt.

When all is dissolved¹ the melted mass is poured into a large, dry platinum dish, what adheres to the two crucibles is removed by diluted sulphuric acid, and the solution, with rinsings, is poured into the dish. Much more dilute sulphuric acid is added and the dish heated till the solid is dissolved. The solution is evaporated as far as can be done on the steam bath, then gradually heated higher till fumes of sulphuric acid come off copiously. During this heating the mass is apt to darken from reduction and separation of dissolved platinum. The acid should have been used in such quantity that after cooling the mass is pasty and not solid, for it then dissolves readily, on heating, in the water which is now to be added, the sodium salt dissolving much more readily than the potassium salt. It is important that the amount of absolute acid used shall be approximately known, so that in the subsequent reduction of iron the volume of the solution can be so adjusted as to contain from 1.5 to 2.5 per cent by volume of acid.

The dish is placed on the bath and soon the silica can be seen in coagulated form at the bottom. It is collected on a small filter, well

large amount of the salt in a platinum dish and keep it in fusion till spattering ceases and white fumes begin to come off freely. If the liquid is then poured out into other dishes it cools in thin sheets or cakes, which can be readily broken up and bottled for future use. With such material the fusion is always tranquil, and the action on the alumina, etc., much more intense and speedy than with the ordinary bisulphate. If a good article of the latter is not to be had by purchase, it is only necessary to mix and melt together equivalent weights of sulphuric acid and pure normal sulphate until the water of the acid has been mostly expelled and the conversion to pyrosulphate accomplished.

The recommendation of J. Lawrence Smith (*Am. Jour. Sci.*, 2d ser., vol. 40, 1865, p. 248) to use the sodium instead of the potassium salt has been followed with satisfaction. This salt acts more quickly and forms a more soluble double salt with aluminum, but has the slight disadvantage that the progress of decomposition of the ignited mass is not so readily followed because of the greater tendency of the sodium salt to crust over.

A further objection is the action on the crucible of the fused pyrosulphate and the consequent necessity of removing the dissolved platinum. To obviate this and likewise to effect more speedy solution of the oxides E. Deussen (*Zeitschr. anorg. Chemie*, vol. 44, 1905, pp. 423-426), fuses the finely powdered oxides with acid potassium fluoride (about 1 gram). The mass melts at first over a low flame, then solidifies. Its solution is evaporated with sulphuric acid to expel most of the fluorine, then reduced with hydrogen sulphide or sulphurous acid and titrated for iron. The use of the fluoride is, however, incompatible with accurate work in silicate analysis, because the silica in the ignited oxides can not be determined. Moreover, the oxides must be finely powdered and consequently an aliquot part only can be taken for the fusion. The expulsion of fluorine by sulphuric acid must furthermore be thorough if titanium is to be determined in this solution.

¹ Should a small portion of the precipitate have escaped solution no particular harm is done. The further treatment is not thereby changed.

washed with hot water, burned, and weighed in a platinum crucible. Being seldom pure, it has to be corrected by a few drops of hydrofluoric and a single drop of sulphuric acid, and the crucible reweighed. The slight residue in the crucible is brought into solution by pyrosulphate and added to the main portion, for the treatment of which see C. a (p. 119) after filtering from barium if present. (See b, below.) The amount of silica recovered thus ranges usually between 2 and 4 mg. after two filtrations of the main silica and is of course to be added to this. Only in this way is the full amount of the silica in the ignited oxides to be recovered.¹ Formerly it was customary to regard that remaining undissolved when the pyrosulphate melt was taken up with water or dilute acid as the total amount present. It is, however, but a small portion of what the alumina held, the greater part having formed alkali silicate during the fusion and remaining in solution afterward, unless set free and rendered insoluble by the treatment above given.

The silica thus recovered does not, however, represent quite all of that which originally escaped separation by evaporation with hydrochloric acid. A small part (roughly 1 to 2 mg. for a single precipitation and a total of 1 centigram of silica in the experiments detailed elsewhere² is not precipitated with the alumina and escapes recovery altogether. It is therefore apparent why a thorough separation of silica at the start is so urgently called for.

In case the recovery of the residual silica is not required, the procedure of W. Trautmann³ for removing it from alumina may be serviceable. He recommends the evaporation of hydrofluoric and sulphuric acids in the crucible containing the ignited alumina, after which the alumina is to be again ignited and weighed. E. Selch⁴ maintains that there is only a negligible loss of aluminum by volatilization as fluoride when this procedure is followed.

b. BARIUM.

Should by any chance the alumina precipitate have held barium sulphate, something which has not happened in my experience with rocks, unless ammonium persulphate was used as in 8. C. a (p. 111), it will be found as a contaminant of the silica recovered after the pyrosulphate fusion. The weighed residue remaining after expulsion of this silica by hydrofluoric acid is dissolved (except the platinum it may have held) by a little pyrosulphate and the cooled melt redissolved in dilute sulphuric acid. Any barium will then be left

¹ For proof see *Jour. Am. Chem. Soc.*, vol. 24, 1902, pp. 368-370; *Chem. News*, vol. 86, 1902, pp. 79, 89.

² *Jour. Am. Chem. Soc.*, vol. 24, 1902, p. 369; *Chem. News*, vol. 86, 1902, p. 90.

³ *Zeitschr. angew. Chemie*, vol. 26, 1913, p. 702.

⁴ *Zeitschr. anal. Chemie*, vol. 54, 1915, p. 395.

in the form of sulphate¹ and can be separated by flotation from the heavier platinum.

C. IRON—TITRIMETRIC DETERMINATION IN THE FERROUS STATE.

a. WITHOUT REGARD TO VANADIUM.

a. Reduction of the iron by hydrogen sulphide.—Into the cool filtrate obtained in B. a, b (pp. 116–118), held in a beaker and containing from 1.5 to 2.5 per cent by volume of free acid, is introduced hydrogen sulphide for the reduction of the iron to the ferrous state and the precipitation of the platinum resulting from the pyrosulphate fusion. This last effect is rendered complete by causing the solution to boil² with continued passage of the gas, whereby the sulphur becomes coagulated and readily filterable. The gas current is not interrupted till the solution has cooled somewhat. This is then filtered³

¹ Some years ago, in a series of analyses of rocks from the Leucite Hills, in Wyoming, there was obtained at this stage, when it was customary to dissolve the melt in cold water preliminary to precipitation of titanium by boiling the neutralized sulphuric solution in presence of sulphur dioxide, a white, more or less flocculent residue which amounted to 1 to 3 per cent of the rock and which was at first taken to be a mixture of tantalic and columbic acids. Eventually, it was found to consist apparently of nothing but TiO_2 and P_2O_5 , with perhaps a little ZrO_2 . By repeated fusion with acid potassium sulphate and leaching with cold water it could be brought gradually into solution. It was these rocks which furnished the most striking instance of the peculiar milky sulphate residues mentioned on page 104 as derived from the ignited silica.

A. Knop (*Zeitschr. Kryst.*, vol. 10, 1885, p. 73) seems to have obtained a similar mixture in analyzing minerals from the Kaiserstuhl in Baden, but its nature was not ascertained, though it was suspected to be, if not silica, columbiferous titanic acid.

² The precipitation of platinum from a hot sulphate solution is far quicker and cleaner than from hydrochloric acid. Further, this platinum sulphide, when ignited in the crucible in which the bisulphate fusion was made, should weigh together with the crucible itself what the latter weighed before the main oxide precipitate was fused in it; in other words, the weight of the platinum recovered by hydrogen sulphide should equal the loss in weight of the crucible due to attack by the bisulphate.

In somewhat rare instances this will not be so, but the weight will be greater, showing a gain in platinum which may amount to a milligram. Tests have shown that this is not due to retention of platinum by the main Al_2O_3 , etc., precipitate; hence, it must come from platinum mechanically loosened from the dish during the drying and powdering of the silica preparatory to its collection on the filter, or to some insoluble compound of platinum formed during evaporation and drying of the silica. It may also be in part or wholly due to contamination from platinum reduced during evaporation of the filtrate from the basic-acetate separation. It will be remembered that from this filtrate a small amount of iron oxide and alumina is recovered and added to the main precipitate. Hence it is always well in fine work to collect the sulphide and weigh the platinum in the original crucible, deducting any excess from the alumina, or else to get rid of the platinum by hydrogen sulphide before proceeding to the precipitation of alumina, etc. (See 7, p. 106.)

³ Through a Gooch crucible lined with asbestos or platinum sponge. A paper filter may be used if first washed with hot water in order to remove a small amount of reducing matter (McBride, R. S., and Scherrer, J. A., *Jour. Am. Chem. Soc.*, vol. 39, 1917, p. 928).

Filtration is not necessary if only precipitated sulphur and no sulphides are in suspension, for the sulphur is without reducing action on cold permanganate solution, as H. L. Wells, and W. L. Mitchell and others before them have pointed out. These authors used this method of reducing ferric iron in titanite ores (*Jour. Am. Chem. Soc.*, vol. 17, 1895, p. 878; *Chem. News*, vol. 73, 1896, p. 123). The observation of A. Coppadoro (*Gazz. chim. ital.*, vol. 31, pt. 2, 1901, p. 217) that the precipitate of sulphur caused by reducing ferric solutions with hydrogen sulphide carries some iron as sulphide, even in strongly acid solutions and after thorough washing, need not be regarded. He seems to have operated on very concentrated solutions as compared with those here in question.

warm into a half-liter flask, hydrogen sulphide is again introduced for a few minutes, with production of slight milkiness if any iron had become oxidized during filtration, the flask is then connected with a carbon-dioxide generator already in action for a time, and the solution brought to boiling to expel the hydrogen sulphide. The expulsion is aided by a rapid current of carbon dioxide,¹ the end point being found by occasional testing of the escaping gas with lead-acetate paper.² When this point is reached, the flame is removed and the flask allowed to cool without interrupting the gas current. The cooling is hastened by placing the flask in a basin of cold water.

β. *Titration of the iron and subsequent treatment of the solution.*—A burette with permanganate solution having been made ready, the gas tube is rinsed into the flask and the permanganate at once run into the latter without further dilution of the solution, which is kept in rotary agitation by an appropriate movement of one hand. The bulk of the solution will be from 100 to 200 cm.³ The drops of the titrating fluid that may fall upon the neck of the flask are washed down by aid of a wash-bottle. The strength of the permanganate solution would best not much exceed 0.0025 gram of iron to the cubic centimeter, for the amounts of iron to be determined are moderate and often very small.³

¹ The gas generated from every new lot of marble must be tested carefully for hydrogen sulphide. Even pure white marble is frequently not free from soluble sulphides—probably pyrrhotite, sphalerite, or galena—and the amount may be enough to affect appreciably the result of titration for iron. A good precaution to take is to wash the gas by passing it through a large U tube containing glass beads and a solution of copper sulphate.

² The test is most delicate when the flask is provided with a two-hole stopper fitted with inlet and outlet tubes of glass. If the outside opening of the outlet tube is small, the concentration of the escaping steam and gas contributes to the sharpness of the test. Because of the possibility of the introduction of organic matter from the stopper by the action of the hot steam, it is safer to employ a cap of platinum foil with two holes, one for the gas entry tube, the other for its escape in a concentrated stream.

If the solution was free from milkiness at the start, the operation of expelling hydrogen sulphide need not take more than 10 to 20 minutes; otherwise a longer time will be required to remove the last traces. The immediate effect of boiling on any moderate amount of suspended sulphur is to coagulate it and clear up the solution completely. Some of the sulphur volatilizes with the steam, but a further portion appears to be converted by it to hydrogen sulphide, so that a faint reaction for that gas can be obtained as long as any sulphur remains. This is probably the explanation for Washington's direction (*Manual of the chemical analysis of rocks*, 1904, p. 112) to boil for about two hours, since by this method of reducing the iron, without coagulating the sulphur, the filtrates are always strongly milky. It is important to bear in mind that excess of hydrogen sulphide at this stage is not proof that all ferric iron has been reduced. Alkali sulphocyanate occasionally reveals the presence of unreduced iron. Due caution therefore renders it advisable to test a drop of the solution and to introduce more hydrogen sulphide if the result shows that it is needed. Experiments made under my direction at the Bureau of Standards by R. S. McBride show that perfect results are to be had only when the acid concentration is kept within very narrow limits. For the average run of rocks these may range from 1.5 to 2.5 per cent sulphuric acid by volume, but for iron ores a variation of even 0.5 per cent from 2 per cent produces a sensible error. Reduction is then incomplete with more than 2 per cent of absolute acid; with less than this amount too much permanganate is required.

³ The permanganate should be standardized against pure sodium oxalate, such as the Bureau of Standards provides. Ferrous sulphate and ferrous-ammonium sulphate are less reliable. Iron wire should not be used under any circumstances.

The results are strictly accurate, with the limitations set forth in b below, when care is taken with the reduction by hydrogen sulphide. The method is superior to that involving the use of zinc, for no foreign impurity affecting the result is introduced and the ever-present titanium is not affected, nor is vanadium reduced below the condition of V_2O_4 , whereas nascent hydrogen converts it in part at least to V_2O_2 .

The solution, after titration, is returned to a dish, which may be of porcelain, and evaporated to a volume of much less than 100 cm.³ if the rock is supposed to carry less than 1 per cent of titanic oxide. For each additional 1 per cent the final volume may be larger by 100 cm.³ The solution is then transferred to a graduated flask having a capacity of 50, 100, 200 cm.³ or more, as the case may be, and enough hydrogen peroxide free from fluorides is added to peroxidize the titanium fully, the flask is filled with water to the mark and well shaken, and the titanium is determined colorimetrically. (See 14. B, p. 155.)

Or, as the presence of large amounts of alkali sulphates is detrimental in the color determination, an ammonia precipitation can be made and the precipitate, after filtering and washing, dissolved in the requisite amount of sulphuric acid. (See 14. B. c, p. 157.)

γ. *Reduction with titanous sulphate.*—H. D. Newton¹ reduces the iron by titanous sulphate, oxidizes the excess of the sulphate by bismuth oxide, and titrates the remaining ferrous salt by permanganate.

The titanous solution is prepared by fusing 20 grams of commercial titanic oxide with alkali carbonate, dissolving the finely ground melt in concentrated sulphuric acid, cooling, diluting somewhat, filtering through asbestos, reducing with zinc, and diluting with about 2 liters of water. The solution is to be kept in a reservoir connected with a burette and a hydrogen generator.

The determination is made as follows: Add to the sulphuric acid solution of the ferric iron in the cold an excess of the titanous solution, destroy the excess with a little bismuth oxide, filter from the excess of bismuth oxide and the precipitated bismuth into cold water, and titrate with permanganate. The titanous solution must be treated in a similar manner in order to be able to correct for an iron content.

Because of the added titanium this method precludes the determination in this solution of the titanium in the rock or mineral.

b. HAVING REGARD TO VANADIUM.

If vanadium is present the value found for iron will be in error, whether the reduction was brought about by hydrogen sulphide, as

¹ Am. Jour. Sci., 4th ser., vol. 25, 1908, p. 343; Chem. News, vol. 97, 1908, p. 218; Zeitschr. anorg. Chemie, vol. 58, 1908, p. 378.

in a. α , or by titanous sulphate, as in a. γ , or by nascent hydrogen. The first of these reagents reduces V_2O_5 to V_2O_4 , which in its action on permanganate solution is equivalent to 2 molecules of FeO . After the first transitory pink blush throughout the liquid, the more slowly acting vanadium may require the addition of a drop or two more of permanganate before a fairly permanent coloration appears.

How far titanous sulphate reduces vanadium is not known to me. If below the V_2O_4 stage, the bismuth oxide, as used in a. γ , may not convert it wholly to V_2O_4 again, for Newton in a private communication stated that vanadium which has been reduced by zinc to V_2O_2 is oxidized by bismuth oxide only to V_2O_3 if the solution is strongly acid (10 per cent H_2SO_4) by volume and cool, but toward V_2O_4 if the solution is warm or less acid.

Nascent hydrogen reduces the higher vanadium compounds to V_2O_2 , which for its conversion to V_2O_5 requires an amount of permanganate equivalent to 6 molecules of FeO .

In view of what has been said, it seems advisable to use only the method of reduction by hydrogen sulphide when vanadium is present. When the amount in the rock is known, a correction can be applied on the assumption that practically all the vanadium is here collected, a point that needs further investigation. Various authors assert its precipitability with alumina and iron by ammonia and ammonium acetate, though Carnot¹ states that repeated precipitation by ammonia, ammonium carbonate, or ammonium sulphhydrate separates it from iron. My experience with ores very rich in vanadium shows that precipitation along with iron and aluminum is only partial. Ridsdale² has determined its precipitability with various metals and gives numerous figures which show an approximation to 90 per cent thus thrown down under the conditions prevailing in analysis of iron slags, the remainder passing into the filtrates and appearing in small part with the lime and to a greater extent with the magnesium phosphate. For all practical purposes it is probably safe to assume that the small amounts of vanadium met with in rocks are wholly in the alumina precipitate.

If the amount of vanadium in the rock is not known and great accuracy is necessary, caution requires the determination of the total iron to be made either in a separate portion or after reprecipitation from the above solution, as follows: Fuse with sodium carbonate, extract with water, bring the insoluble residue into sulphuric solution, reduce, and titrate as above directed. But unless a certain precaution is here observed an error greater than that which it is designed to avoid will be committed. Contrary to general belief, the aqueous extract from the sodium-carbonate fusion carries a small

¹ Compt. Rend., vol. 104, 1887, p. 1803; Zeitschr. anal. Chemie, vol. 32, 1893, p. 223.

² Jour. Soc. Chem. Industry, vol. 7, 1888, p. 73.

but appreciable fraction of 1 per cent of iron, as I have found repeatedly by actual test. This iron is thrown out with the alumina (and silica, if present) by the usual methods of neutralizing the alkaline solution, and can be brought to light when the precipitate thus formed is treated with a fixed caustic alkali, or again fused with sodium carbonate and leached with water, when it remains wholly or in part undissolved. Hence it is necessary to collect this iron and add it to the main portion before titration.

The differential method of Graham Edgar¹ for determining iron and vanadium in presence of each other is not well suited to rocks, because of the very small amounts of vanadium involved.

C. TRUE VALUE FOR FERRIC IRON.

The total iron in the rock having been found in one way or another, it remains to deduct an amount equivalent to the ferrous oxide the rock contains and a further amount corresponding to the sulphides often present, in order to get what may pass for the true value for ferric iron. That this is often only an approximation appears from the difficulties due to the presence of vanadium and the generally indeterminable effect of sulphides on the ferrous-oxide determination. (See pp. 201-202.)

D. IRON—TITRIMETRIC DETERMINATION IN THE FERRIC STATE.

a. PRELIMINARY REMARKS.

Chemists have long felt the want of a method for determining ferric iron directly by titration, both for the purpose of avoiding prior reduction to the ferrous state and as a check on the ferrous iron determination, especially when the metal exists in both states side by side. The method given below would seem to be applicable to the mixture of oxides obtained as under 8 (pp. 106-113), but its applicability to the direct determination of ferric iron in rocks has not been studied. If suitable for minerals that are readily soluble in sulphuric or hydrochloric acid, it might not be so for rocks, for these would have to be attacked by hydrofluoric acid with exclusion of air (21. d, p. 203), the resulting condition being then quite different from the conditions under which the authors of the method worked.

b. TITRATION WITH TITANOUS CHLORIDE.

E. Knecht and Eva Hibbert² titrate with a solution of titanous chloride of about 1 per cent strength. For standardizing this solution they used a ferric solution prepared from ferrous ammonium sulphate, with potassium thiocyanate as indicator, added directly

¹ Am. Jour. Sci., 4th ser., vol. 26, 1908, p. 9.

² Ber. Deutsch. chem. Gesell., vol. 36, 1903, p. 1549.

toward the end of the titration or used preferably in spot tests. With the standard a ferric solution of unknown content is titrated in the same way.

If ferrous and ferric salts are present together the solution is first titrated with permanganate for the ferrous iron and then with titanous chloride for the total iron.

E. IRON—GRAVIMETRIC DETERMINATION AFTER SEPARATING AS SULPHIDE.

a. PRELIMINARY REMARKS.

In view of the slight errors involved in the titrimetric determination of the iron it may be advantageous occasionally to determine it gravimetrically as the oxide, after first precipitating as the sulphide from a solution containing ammonium tartrate, the function of which is to hold in solution the other elements. If manganese, nickel, and cobalt are not present, this method yields a pure product. If manganese is present the purity of the resulting iron oxide will depend upon the amount of manganese and whether the iron hydroxide was precipitated by ammonia or by sodium or ammonium acetate. If there is doubt the purity of the final product can be determined by a colorimetric test for manganese (11. C, p. 137). The procedure does not admit of conveniently determining titanium colorimetrically, as in the method described in 9. C (p. 119).

b. PROCEDURE.

In the filtrate from the residual silica (9. B. a, p. 116), which should be brought to a volume of 100 to 400 cm.³, according to the amount of iron present, and held in a flask or beaker, is dissolved tartaric acid (3 to 4 times the weight of the oxides operated upon). In order to provide the best conditions for the next step the solution is made neutral with ammonia and acid again with 2 cm.³ of sulphuric acid (1:1). Hydrogen sulphide is then introduced until the solution has become colorless, the iron being then reduced to the ferrous state. If not reduced in acid solution before the next step is taken there is a possibility of precipitating a little titanium.¹ The solution is then made decidedly ammoniacal, and more hydrogen sulphide is introduced. After the ferrous sulphide settles in the corked flask or covered beaker, it is filtered and washed thoroughly with water containing a little ammonium sulphide and enough ammonium chloride (sulphate if the preliminary operations noted under 10. B, p. 126, are to follow) to prevent passage of the filter by colloidal iron sulphide. The funnel should be kept covered as much as possible, and the precipitate finally sucked fairly dry.

Precipitate and paper are then placed in a beaker of suitable size, hydrochloric acid (1:1) is added, the vessel being covered, and heat

¹ Cathrein, A., *Zeitschr. Kryst.*, vol. 6, 1882, p. 243; vol. 7, 1883, p. 250.

is applied until all black particles have disappeared. The paper is then shredded by vigorous stirring with a rubber-tipped glass rod, the iron is oxidized by a few drops of nitric acid, the solution diluted if necessary, and the iron precipitated by ammonia. As aluminum is absent it is not necessary to avoid overstepping neutrality.

As soon as the precipitate has settled it is filtered, washed only a few times with hot water, sucked dry, wrapped in its paper, and placed moist in a weighed platinum crucible, the paper is carefully charred, and when the carbon has disappeared the full heat of the burner or of a blast of moderate power is applied for 5 to 15 minutes according to the weight of the oxide.

The filtrate from the iron sulphide can be treated as in the first paragraph of 10. B and then in a variety of ways, either directly as given under 10. B or by suitable application of the procedure indicated under 10. C, D, and E (pp. 127-132), 14 (p. 154), and 16 (p. 172).

F. IRON—SPECIAL CASES.

a. GLASS SANDS.

Materials used in making certain kinds of glass, especially optical glass, should contain no more than a very minute amount of iron. For the iron determination in glass sands it is customary to attack the sand with hydrofluoric and sulphuric acids until the silica disappears, whereupon heat is applied to drive off the excess hydrofluoric acid and most of the sulphuric acid. J. B. Ferguson¹ has drawn attention to the fact that this procedure fails to decompose certain minerals in these sands that are iron-bearing, like magnetite, ilmenite, tourmaline, and staurolite, and that the iron reported represents but a part of that actually in the sand. He points out properly that the slight residue left on treating the sand with hydrofluoric and sulphuric acids and evaporating till white fumes appear should be collected on a filter paper and treated further, as follows:

The residue left after igniting the filter is fused with a little iron-free potassium pyrosulphate. If after the melt is dissolved in dilute sulphuric acid no dark particles are to be seen, the operation is ended. If dark particles (staurolite) are still evident, they are to be collected on a filter, ignited, and fused with sodium carbonate free from iron. The sulphuric acid solution of the melt should show no undecomposed matter. The filtrates are combined for the iron determination.

Ferguson prefers to reduce the iron with stannous chloride and then to titrate with bichromate, determining the end point electro-

¹ Jour. Ind. Eng. Chemistry, vol. 10, 1918, p. 941.

metrically as suggested by J. H. Hildebrand,¹ and for this reason dissolves the fusions in hydrochloric acid (1:1) instead of sulphuric acid.

Needless to say, freedom of the reagents used from iron and the use of a platinum crucible that is also iron free are of prime importance. Blank runs on the reagents will eliminate the error due to an iron content if the work is very carefully done, but such correction is not entirely safe.

b. CERAMIC CLAYS.

For clays low in iron J. W. Mellor² uses a colorimetric method based on the color imparted to an ether-amyl alcohol solution of ferric iron by potassium thiocyanate.

10. MISCELLANEOUS SEPARATIONS OF THE OXIDES OBTAINED UNDER 8.

A. PRELIMINARY REMARKS.

Although, as said in 9. A, it is customary to determine aluminum by difference, special cases may call for treatments that are different from those recorded in the foregoing section. Thus it may happen, though not in ordinary rock analysis, that only a very small amount of aluminum is present, and that a direct determination of it is necessary or desirable in order to ascertain its amount with greater certainty than is possible by the method of difference or even to determine whether it is actually present. Again, in view of the errors incidental to the colorimetric determination of titanium, it may be desired to determine this element with greater precision than is possible in the presence of much iron and alkali salts, in which case the procedures allowable will enable one to take account of zirconium also.

A direct determination of aluminum is feasible by the procedures given below only when phosphorus is absent. It is possible when titanium and zirconium are present, but then further operations are called for.

As to phosphorus, see second paragraph under 9. A (p. 116).

In addition to the procedures that follow others will be found in the sections on phosphorus (p. 177) and chromium (p. 180).

B. RECOVERY OF ALUMINUM, TITANIUM, ZIRCONIUM, AND PHOSPHORUS FROM THE FILTRATE FROM IRON SULPHIDE.

The filtrate from the iron sulphide obtained according to 9. E. b (p. 124), containing ammonium tartrate, is evaporated in a large platinum dish with 10 to 12 cm. of strong sulphuric acid and heated carefully until charring and frothing have continued as far as the capacity of

¹ Jour. Am. Chem. Soc., vol. 35, 1913, p. 871. Consult Hostetter, J. C., and Roberts, H. S. Jour. Am. Chem. Soc., vol. 41, 1919, p. 1337, for application of the method to the determination of iron.

² Pottery Gaz., vol. 34, 1909, p. 1178; Quantitative inorganic analysis, p. 200, 1913.

the dish permits. After cooling 5 cm. of fuming nitric acid is added, and when violent reaction has ceased the heat is raised gradually until the organic matter is fully oxidized.¹ The residue is dissolved in water, and the aluminum and phosphorus, together with titanium and zirconium, if these are present, are precipitated by ammonia according to 8. B. a (p. 106), redissolved, and again precipitated, filtered, washed, and weighed. Further separations will then be in order by one or another of the procedures described below, the absence of rare earths being assumed.

1. A precipitate containing aluminum, titanium, and zirconium and free from silicon may be fused with sodium carbonate or sodium carbonate and borax (C, below) and the aluminum determined in the aqueous extract of the melt, the other components in the insoluble residue. (See sections 14 and 15.) But if phosphorus is also present it goes with the aluminum into the extract. Then, when the aluminum is precipitated by ammonia after acidifying with hydrochloric or nitric acid, phosphorus will accompany the aluminum and must be determined separately in the ignited and weighed precipitate of Al_2O_3 and P_2O_5 . Thus finally the aluminum is found by difference. If chromium and vanadium are also present, other modifications must be introduced.

2. A first variant of the foregoing procedure, after destroying the ammonium tartrate, is to precipitate titanium and zirconium by "cupferron" (14. C. b, p. 162). Vanadium, if present, will be partly precipitated, phosphorus only slightly.

3. A second variant is to evaporate the ammonium tartrate filtrate from the iron sulphide to dryness in a large platinum dish without the addition of sulphuric acid, to char the residue and fuse it with sodium carbonate and nitrate, extract with water, and filter. Titanium and zirconium are left on the filter as sodium salts, while chromium and vanadium are carried into the filtrate as chromate and vanadate along with aluminum and phosphorus. The further separation of the last two from chromium and vanadium is outlined under 18. B (p. 178).

As with the other methods, this is as far as the separation can be carried. The aluminum must still be found by subtracting the P_2O_5 (separately determined) from the combined weights of the Al_2O_3 and P_2O_5 .

C. DIRECT FUSION OF THE OXIDES OBTAINED UNDER 8 WITH SODIUM CARBONATE AND BORAX.

A procedure tried by L. Weiss and H. Kaiser² for separating aluminum from titanium and iron is applicable probably also when phosphorus and zirconium are present. The weighed oxides are

¹ Thornton, W. M., *Am. Jour. Sci.*, 4th ser., vol. 34, 1912, p. 214.

² *Zeitschr. anorg. Chemie*, vol. 65, 1910, p. 345.

fused over the blast with twenty times their weight of a mixture in equal parts of sodium carbonate and borax. To the clear fusion is added half the former weight of flux, and when this is melted the mass is cooled and let stand for 24 hours in cold water. After filtering, the fusion and extraction are repeated on the residue, if necessary. The authors claim complete separation of aluminum in this way. If silicon is present they remove it before the alkali fusion by treating the mixed oxides with sulphuric and hydrofluoric acids.

In this treatment phosphorus should accompany the aluminum, and zirconium the titanium and iron. Further separations and eventual determinations can be made in ways that have been given for iron or are to be consulted in the sections on titanium and zirconium.

D. SEPARATION OF ALUMINUM, TITANIUM, AND ZIRCONIUM FROM IRON IN THE FERROUS STATE.

a. BY PHENYLHYDRAZINE.

A method for the "direct determination of alumina in presence of iron, manganese, calcium, and magnesium" is that of Hess and Campbell,¹ but, as with the methods just considered, it involves finally weighing aluminum, phosphorus, titanium, and zirconium together. Precipitation is made by phenylhydrazine, after first neutralizing the (preferably chloride) solution by ammonia and reducing iron by a saturated solution of ammonium bisulphite. Phenylhydrazine "precipitates aluminum from its solutions quantitatively as the hydroxide without a trace of the precipitate being redissolved in excess of the precipitant."

E. T. Allen investigated the method in the Survey laboratory² and confirmed the above authors' statements in the main, finding, however, that two precipitations are needed to free the precipitate entirely from iron. "The method is excellently adapted to the separation of very small quantities of aluminum, such as a milligram or even less, from a large excess of iron, a point of considerable practical importance."

Although such conditions will not be met with in ordinary rock analysis, it will not be out of place here to give the treatment as slightly modified by Allen:

The volume of the solution may vary, according to the quantity of alumina to be precipitated, from 100 to 200 cm.³ It should be heated and reduced by adding saturated ammonium bisulphite. From 5 to 20 drops, according to the quantity of iron, may be used. If the solution turns deep red (ferric sulphite), it is not acid enough, and a few drops of hydrochloric acid should be added, for the sulphite itself does not reduce ferric salts, at least not with rapidity. Now, quickly

¹ Jour. Am. Chem. Soc., vol. 21, 1899, p. 776; Chem. News, vol. 81, 1900, p. 158.

² Jour. Am. Chem. Soc., vol. 25, 1903, p. 421.

bring to neutrality with ammonia, and then add several drops of dilute hydrochloric acid. If this last operation is done too slowly the oxygen of the air helps to form a little ferric hydroxide, which does not always readily dissolve in the dilute acid. Finally, add from 1 to 3 cm.³ of phenylhydrazine,¹ according to the weight of the alumina to be precipitated. If too little has been used, a few drops added to the filtrate will disclose the mistake. Stir until the precipitate has become sufficiently flaky and allow to settle. The supernatant liquid will now be plainly acid to litmus. One need not be disturbed if the precipitate has a brownish color, for it is not due to ferric hydroxide but to the coloring matter contained by all phenylhydrazine which has not been freshly distilled. When the determinations are allowed to stand too long the air increases this oxidation product, and a brown insoluble scum forms on the surface of the liquid and on the sides of the vessel, which is rather troublesome to the analyst. Fortunately equilibrium appears to be established in a short time. The vessels need not stand more than an hour, at any rate. The precipitate is washed by a solution of phenylhydrazine sulphite made by adding cold saturated sulphurous acid to a little phenylhydrazine until the crystalline sulphite first formed dissolves in the excess. The solution has an acid reaction. Five to 10 cm.³ of this are used in 100 cm.³ of hot water.

b. BY SODIUM ACETATE.

α. According to Dittrich and Freund.—M. Dittrich and S. Freund² found that the separation of titanium and zirconium from iron by sodium acetate could be made perfect if the iron was first reduced and then kept in the ferrous state. In another paper³ they apply it also to the separation of thorium.

The acid solution of the pyrosulphate fusion of the mixed oxides is treated with hydrogen sulphide, to reduce the iron, and filtered. The acid is neutralized by adding a solution of sodium carbonate, whereby the formation of black ferrous sulphide serves as an indicator. Then a few drops of dilute sulphuric acid are added and more hydrogen sulphide is passed in to complete the reduction of the iron. The solution is brought to boiling while a current of carbon dioxide is made to pass until every trace of hydrogen sulphide is expelled. A concentrated solution of 5 grams of sodium acetate is added, followed by hot water to make a volume of 400 to 500 cm.³ Boiling and continued passage of carbon dioxide are kept up for an hour, with replacement of the escaping water. The liquid is then cooled while the gas current continues. The white precipitate is filtered and washed with water charged with a little hydrogen sulphide. Precipitate that adheres to the glass is removed by a few drops of concentrated sulphuric acid and a little hydrogen peroxide, precipitated by ammonia after destroying the excess of peroxide, and added to

¹ The reagent should, of course, be free from inorganic impurities which could disturb the results. The author [Allen] found one sample which after persistently giving high results was proved to contain tin, which had probably been used in its preparation.

² Zeitschr. anorg. Chemie, vol. 56, 1907, p. 337.

³ Idem, p. 348.

the main portion. The whole is then ashed and weighed. After fusing with pyrosulphate and dissolving in water, any silica that may have separated is filtered off and weighed.¹ Titanium is then determined colorimetrically and zirconium found by difference. It is better, if zirconium is relatively in very small amount, to determine this according to 16. A (p. 173) and the titanium by difference or by colorimetry (14. B, p. 155).

The iron can be precipitated by ammonia in the filtrate after it has been oxidized.

The method was applied by Dittrich and Freund in absence of aluminum and phosphorus, but in view of the reported success of the method which is next described the presence of aluminum may not be detrimental. It should be borne in mind, however, that the precipitation of aluminum by sodium acetate as ordinarily done is not supposed to afford as perfect a separation of that element as of iron.

β. *According to Barbier.*—P. Barbier² successfully applied a very similar method to the separation of aluminum from iron in analyzing many minerals, the reducing agent being sodium hyposulphite ($\text{Na}_2\text{S}_2\text{O}_4$) instead of sodium bisulphite.

To the hydrochloric acid solution a slight excess of sodium hyposulphite is added until the liquid takes on a reddish tint. A 10 per cent solution of sodium hyposulphite is then added, little by little, until the red color disappears. The solution is boiled, whereupon the aluminum separates as a dense powder entirely free from iron and easy to filter and wash. The precipitate and paper are ashed, after moistening with nitric acid. If glucinum is present it accompanies the aluminum. Probably titanium and zirconium would be precipitated also and could be determined by one or another of the methods given in their respective sections. No analytical data are given by Barbier. The reagent is unstable and is subject to contamination, particularly by zinc.

E. SEPARATION OF TITANIUM AND ZIRCONIUM FROM ALUMINUM AND IRON.

a. ACCORDING TO BASKERVILLE.

A method devised by C. Baskerville³ for separating jointly titanium and zirconium from aluminum and iron is claimed by A. J. Rossi⁴ to be the best gravimetric method for the precipitation of titanium and its separation from iron and aluminum. It has also given very good results in the laboratory of the Bureau of Standards. The method succeeds in hydrochloric but not in

¹ If silica is present, however, its recovery is imperfect unless the operation is conducted as detailed in 9. B. a (p. 116).

² Bull. Soc. chim., vol. 7, 1910, p. 1027.

³ Jour. Am. Chem. Soc., vol. 16, 1894, pp. 427, 475.

⁴ Titanium in steel, 1911, p. 38, quoted by B. Neumann and R. K. Murphy in Zeitschr. angew. Chemie, vol. 26, 1913, p. 613.

sulphuric acid solution, and is therefore not directly applicable to the solution of the oxides obtained as described under 9. B. a (p. 116). If it is desired to apply this method to that solution after separating silica, an ammonia precipitation must be made and the precipitate dissolved in hydrochloric acid after filtering and washing.

In the second of his two papers Baskerville, in describing the method as applied to zirconium, states that it is necessary to neutralize the solution with ammonia until the precipitate formed no longer dissolves on boiling, to effect re-solution of it by two or three drops of hydrochloric acid, and to boil for two minutes after adding an excess of sulphur dioxide. As the precipitate may contain a little iron, it should be dissolved after filtering and reprecipitated as before.

If both titanium and zirconium are present, these must be separately determined according to 14. B (p. 155) for titanium and 16. A (p. 173) for zirconium. If nothing but the two oxides is present and one of these is in great excess over the other, it may suffice to determine directly only the lesser and to obtain the other by difference. Phosphorus will also be precipitated if not in excess. Further reference to this method appears under 14. C. c (p. 166).

D. ACCORDING TO DITTRICH AND FREUND.

Of several methods proposed by M. Dittrich and S. Freund,¹ by which they claim to separate completely titanium and zirconium from iron, they regard the one given below as relatively the simplest. It presupposes, however, a prior fusion of the mixed oxides with potassium hydroxide in a silver crucible, in order to remove aluminum and phosphorus, an operation which involves a probable error as pointed out in the next section, F.

The sulphate solution is reduced by hydrogen sulphide, filtered into a 750 cm.³ Jena flask provided with a stopper carrying inlet and outlet tubes and a separatory funnel. The solution is now neutralized with sodium carbonate, the formation of ferrous sulphide serving as indicator, a few drops of sulphuric acid are added, and hydrogen sulphide is passed in to complete the reduction of the iron. The gaseous reagent is then wholly removed by carbon dioxide at boiling heat, whereupon a concentrated solution of 5 to 10 cm.³ of ammonium sulphate is allowed to flow in, followed by water, if needed, to make the volume 400 to 500 cm.³. With continued passage of carbon dioxide and renewal of escaping water the solution is now boiled for about an hour, then cooled. The white precipitate is filtered and washed with hot water slightly charged with hydrogen sulphide. A few drops of sulphuric acid and hydrogen peroxide are used to cleanse the walls of the flask, and the titanium and zirconium thus dissolved

¹ Zeitschr. anorg. Chemie, vol. 56, 1907, p. 337.

are precipitated by ammonia and added to the main portion, the whole being ignited in platinum over the blast to constant weight. The oxides are fused with potassium bisulphate; silica, derived from the reagents or apparatus, is separated (9. B. a, p. 116); and titanium and zirconium are determined, the one colorimetrically, the other by difference. In view of the very small amounts of zirconium in rocks it is far preferable to find it directly (16. A, p. 173) instead of by difference.¹

In the filtrate from the oxides Dittrich and Freund precipitate iron and manganese by ammonia and hydrogen peroxide.

F. SEPARATION OF ALUMINUM FROM IRON, ETC., BY A FIXED CAUSTIC ALKALI.

A favorite practice in some countries of Europe has been to fuse the ignited precipitate containing Al_2O_3 , Fe_2O_3 , TiO_2 , P_2O_5 , etc.—or that of the Al_2O_3 , TiO_2 , P_2O_5 , etc., after separation of iron by ammonium sulphide in tartrate solution—with sodium hydroxide in a silver crucible, or to boil the freshly precipitated mixture with a solution of the alkali, on the assumption that the oxide of titanium is hereby rendered wholly insoluble and thus separated from the alumina. This, however, is in part an error long since pointed out by F. A. Gooch,² who showed that pure titanate is markedly soluble under both conditions of treatment. Experiments made by me to test the extent of this error brought out the following interesting results:

When 0.045 gram of titanate was fused by itself with sodium hydroxide, the clear aqueous extract of the fusion held 0.0031 TiO_2 , or about 7 per cent, determined colorimetrically. When freshly precipitated and boiled with the alkali, the solubility was less. When fused with sodium carbonate but an infinitesimal trace was dissolved, which required strong concentration for its detection. When mixed with a large excess of alumina and fused with the caustic alkali, the solubility was still very marked, though less than when alumina was absent. With a large excess of ferric oxide, with or without alumina, no titanium could be detected in the unconcentrated filtrate.

It thus appears that fusion with caustic alkali after first removing iron involves an error in the gravimetric determination of both aluminum and titanium which does not appear if the iron has not been removed. The procedure of M. Dittrich³ involves this error and therefore is not described here.

¹ The newer method of Dittrich and Freund (*Zeitschr. anorg. Chemie*, vol. 56, 1907, p. 344), by which zirconium is precipitated as the salicylate and ignited to the oxide, may find application here.

² *Proc. Am. Acad. Arts and Sci.*, vol. 12, 1885, p. 436; *Bull. U. S. Geol. Survey*, No. 27, 1886, pp. 16, 17.

³ *Anleitung zur Gesteinsanalyse*, 1905, pp. 9–31.

G. SEPARATION OF IRON FROM ALUMINUM, ETC., AS VOLATILE CHLORIDE.

F. A. Gooch¹ and some of his students have modified an old method for separating iron completely from aluminum, zirconium, glucinum, and chromium by volatilizing it as ferric chloride at a lower temperature than was formerly thought to be necessary. The results they obtained are excellent. Presumably an equally good separation from titanium could be effected.

The mixed oxides, put in porcelain boat which is placed in a wide combustion tube heated in a small furnace, are submitted to the action of dry hydrochloric acid gas, generated by dropping sulphuric acid upon a mixture of strong hydrochloric acid, common salt, and a small amount of manganese dioxide. The gas is admitted at one end of the combustion tube and passed out at the other through a water trap, while the required temperature, best 200° to 300°, is maintained by regulating the burners of the furnace. The time of action varies somewhat with the condition of the oxide to be volatilized and the temperature. Generally an hour's heating at 200° proves sufficient for the complete removal of 0.1 gram of iron. At higher temperatures the action is more rapid; but the nonvolatile oxide is liable to mechanical loss if the volatilization of the iron is too rapid. It is better, therefore, to make use of a lower temperature until the volatilization of iron is nearly complete, and then to raise the heat for a few minutes to insure the removal of the last traces of the volatile chloride.

H. Borck² claims to effect a perfect separation of iron from aluminum by heating the mixed oxides in a current of hydrochloric acid vapor and air.

H. SEPARATION OF IRON FROM TITANIUM BY HYDROGEN PEROXIDE.

A. Classen's method³ of separating titanium from iron by hydrogen peroxide succeeds well, according to K. Bornemann and H. Schirmeister⁴ when carried out as follows:

To the acid solution containing a considerable excess of hydrogen peroxide (the pure article "perhydrol" should be used) a solution of potassium hydroxide is added till the iron is fully precipitated as hydroxide. The solution should be cold, and the peroxide should always be in excess. The precipitate when settled is filtered and washed with cold water containing a little peroxide. In order to determine the titanium in the filtrate the excess peroxide is destroyed by sulphur dioxide, disappearance of the color of the peroxidized titanium being the test of its complete reduction. The titanium is then precipitated twice by ammonia. The method is said to be especially good for small amounts of titanium in company of much iron, which in turn is precipitated by ammonia after dissolving in acid, filtered, washed, and weighed.

¹ Methods in chemical analysis, New York, John Wiley & Sons, 1912.

² Zeitschr. angew. Chemie, vol. 25, 1912, p. 719.

³ Ber. Deutsch. chem. Gesell., vol. 21, 1888, p. 370.

⁴ Metallurgie, vol. 7, 1910, p. 726.

Classen says regarding his method that if aluminum is present it is incompletely separated from the iron by the caustic alkali. Further, that when the attempt was made to use ammonia instead of a caustic alkali, the aluminum was not all precipitated, and that if ammonium carbonate was used no precipitation of aluminum took place.

11. MANGANESE, NICKEL, COBALT, COPPER, AND ZINC.

A. DIFFICULTIES IN THE WAY OF A CORRECT GRAVIMETRIC DETERMINATION OF MANGANESE.

The gravimetric determination of manganese in small amounts seems to be more of a stumbling block to the average chemist than that of almost any other of the frequently occurring elements met with in mineral analysis. This is due almost always to incomplete prior separation of elements which later suffer coprecipitation with the manganese. The error is therefore generally a plus one, and often amounts to many times the weight of the manganese actually present. The importance of thorough separation of the constituents treated of in the foregoing pages is therefore manifest, particularly since to the inexperienced analyst very small amounts of manganese precipitated in the form of a higher hydroxide may easily mask a good deal of alumina or other colorless precipitates.¹

¹ It is for these reasons that Washington deems it better for the novice in rock analysis to make no attempt to determine the manganese, but to allow the error from this neglect to distribute itself over the alumina, lime, and magnesia. The relative order of this distribution was determined by George Steiger in the Survey laboratory while analyzing a series of carbonate rocks, some of them highly siliceous. The results are instructive. Double precipitations were the rule, and iron and aluminum were thrown out by ammonia in slight excess, according to the procedure then followed.

Tests showing distribution of manganese in gravimetric separations.

No.	Partial composition of rock.			MnO by colorimetry.			
	Al ₂ O ₃ , Fe ₂ O ₃ .	CaO.	MgO.	Total.	With—		
					Al ₂ O ₃ , Fe ₂ O ₃ (by difference).	CaO.	Mg ₂ P ₂ O ₇ .
957.....	2.03	10.60	6.30	0.193	0.085	0.011	0.097
973.....	9.35	11.84	2.81	.311	.036	.023	.252
974.....	4.80	50.51	1.04	.700	.301	.087	.312
975.....	12.71	11.98	4.30	.442	.088	.016	.338
1126.....	.58	30.54	20.41	.281	.030	.030	.221
1128.....	.98	29.69	19.07	.245	.019	.055	.171
1130.....	3.49	3.99	.92	.016	.016	None.	None.
1131.....	1.00	28.04	19.11	.574	.032	.101	.441

The results in 974 and 1130 particularly show how the manganese once precipitated tends to remain with the alumina, presumably by reason of its having become peroxidized.

According to Steiger, the present practice in the Survey follows to a degree that of Washington, assuming a method of precipitating aluminum, etc., that does not also precipitate manganese. The procedure is to determine total manganese by colorimetry in a separate portion of the sample and to correct the magnesium pyrophosphate for its manganese content by another colorimetric determination. This correction is the more permissible because, as the table above shows, the major part of the manganese remains in solution until precipitated as phosphate with the magnesium, and the error thus thrown upon the alumina and lime is slight. Indication of contamination of ignited calcium oxalate by even very little manganese is revealed usually by a brownish discoloration, sometimes by the green color of calcium manganate.

If the directions already given have been carefully followed, however, there will be little chance of error due to foreign contamination, by either alumina or magnesia, a sufficiency of ammonium salts being a guaranty against the latter. Regard must be had, however, to the rather remote possibility of the presence of rare earths which were not thrown out by the basic-acetate precipitation (see footnote, p. 119), for they will appear at this stage.

B. PRECIPITATION OF THE GROUP AND SEPARATION OF ITS CONSTITUENTS.

1. THE AMMONIUM-SULPHIDE METHOD.

α. Its advantages and disadvantages.—On the other hand, the usual methods of separation of manganese from the alkaline earths and magnesia by bromine or ammonium sulphide are imperfect, in part by reason of incompleteness, in part because of coprecipitation of small amounts of these metals. The former error, though absolutely slight, is probably of more consequence in rock analysis than the latter. In regard to completeness of precipitation bromine offers no advantage over ammonium sulphide, and the latter has the advantage that by a single operation nickel, cobalt, copper, and zinc, if present, are likewise separated from the earth metals and alkalies. There need be no fear of overlooking nickel or copper, for under the conditions of the precipitation they are not retained in solution. It is for this reason chiefly that the ammonium-sulphide method is to be preferred. Most of the small amount of manganese that escapes precipitation is weighed later with the magnesium as pyrophosphate and can be corrected for readily by the colorimetric method described on page 137.

The precipitation of manganese in alkaline solution by hydrogen peroxide, as proposed by P. Jannasch and E. v. Cloedt,¹ a method which appeared to be simple and accurate, besides affording a separation from zinc, was shown by C. Friedheim and E. Brühl² to be valueless.

β. Precipitation by ammonium sulphide and separation of manganese and zinc from nickel, cobalt, and copper.—Two or three cm.³ of ammonia are added to the flask containing manganese, the earth metals, etc. (S. D. a and b, p. 113), and hydrogen sulphide gas is introduced to saturation, whereby manganese, nickel, cobalt, copper, zinc, and a small part of the platinum from the dish are precipitated. A second like amount of ammonia is now added. The flask, filled to the neck and corked, is set aside for at least 12 hours, and preferably 24, or even longer. The precipitate, collected and washed

¹ Zeitschr. anorg. Chemie, vol. 10, 1895, p. 405.

² Zeitschr. anal. Chemie, vol. 38, 1899, p. 681.

on a small filter with water containing ammonium chloride and sulphide, is extracted by hydrogen-sulphide water acidified with one-fifth its volume of hydrochloric acid (sp. gr. 1.11), manganese and zinc, if present, going into solution.

(For treatment of the ammonium-sulphide filtrate see 12. B, p. 144.)

b. MANGANESE AND ZINC.

The hydrochloric-acid filtrate is evaporated to dryness, ammonium salts are destroyed by evaporation with a few drops of sodium-carbonate solution, hydrochloric acid and a drop of sulphurous acid are added to decompose excess of carbonate and to dissolve precipitated manganese, and the latter is precipitated at boiling heat by sodium carbonate after evaporation of the hydrochloric acid. If zinc is present it can be separated from the manganese after weighing. For the small quantities of manganese usually found the sodium-carbonate method of precipitation is to be preferred to that by bromine or sodium phosphate, as equally accurate and a time saver.

The manganese is weighed as Mn_3O_4 and calculated to MnO , or, if present in some quantity, it may preferably be weighed as the sulphate,¹ or, finally, it may be determined colorimetrically with much greater certainty, as in C, below, when the amount is within the usual limits for rocks. In the last case, in the absence of zinc, the hydrochloric-acid solution of the sulphide may be used for the colorimetric test, after first evaporating off the hydrochloric acid with nitric or sulphuric acid.

c. NICKEL, COBALT, AND COPPER.

The paper containing nickel, cobalt, and copper is incinerated in porcelain, the ash is dissolved in a few drops of aqua regia, and the solution evaporated with hydrochloric acid; the copper and platinum are thrown out warm by hydrogen sulphide, and in the filtrate made ammoniacal nickel and cobalt are thrown down by hydrogen sulphide. This liquid is then rendered faintly acid by acetic acid and allowed to stand. The sulphide precipitate after filtering is burned and weighed as oxide—its weight being always very small, hardly ever over 0.3 or 0.4 mg.—which is then tested for cobalt in the borax bead. The color of the last drop or two of the hydrochloric-acid solution, after decomposing the aqua regia, is a good indication of the presence or absence of nickel and cobalt. It is always well at this point to separate by ammonia any traces of iron that may be present, then to acidify and treat with hydrogen sulphide as above.

It is somewhat unsafe to consider traces of copper found at this stage to belong to the rock if the evaporations have been conducted,

¹ Volhard, J., *Ann. Chemie*, vol. 198, 1879, p. 329. Gooch, F. A., and Austin, Martha, *Am. Jour. Sci.*, 4th ser., vol. 5, 1898, p. 209; *Zeitschr. anorg. Chemie*, vol. 17, 1898, p. 264.

as is usually the case, on a copper water or steam bath, or if water has been used which has been boiled in a copper kettle, even if the kettle is tinned inside. Therefore, and because of its contamination by a little platinum, it is better to determine copper in a separate portion if its presence is indicated with certainty. (See 7, p. 106.) This warning is particularly to be heeded if copper or brass sieves were used in preparing the sample.

C. COLORIMETRIC DETERMINATION OF MANGANESE.

a. PRELIMINARY TREATMENT.

As has been shown above (p. 134), the gravimetric determination of manganese is subject to grave error, even when great care is used. This is due to a variety of reasons, such as incompleteness of separation from aluminum and iron, incomplete precipitation by ammonium sulphide, and contamination by other bodies. Because of the small amounts in question these errors may be relatively enormous, and they can not be depended on to balance each other. Therefore, it would be an advance if the total manganese could be determined in a separate portion of the sample, and in the main portion only that part which is weighed with the magnesium pyrophosphate, and this only as a correction to the magnesia. This course is readily feasible with carbonate rocks, which can usually be brought into a fit state in a few minutes without a fusion or the separation of silica. With silicate rocks more labor is involved, but the determination itself is very accurately performed by colorimetry, as in the case of carbonates.

The preliminary treatment consists in decomposing a gram or half a gram of the rock powder in a small platinum dish or capacious crucible (placed in the radiator shown in fig. 2, p. 33) with hydrofluoric and sulphuric acids till all is disintegrated. The hydrofluoric acid is then to be driven off by repeated evaporations with small portions of sulphuric acid, after which either sulphuric or nitric acid free from chlorine is added, together with water, and as much of the residue is brought into solution as possible. What remains insoluble is usually barium and calcium sulphates. This is filtered off on a small filter, the filtrate is caught in a small beaker or flask, and the manganese determined as in the following paragraphs.

b. COLORIMETRIC DETERMINATION OF MANGANESE BY AMMONIUM PERSULPHATE.¹

The use of ammonium persulphate for the colorimetric determination of manganese has the advantage over that by lead peroxide in that, unless chlorides happen to be in the solution, no filtration is necessary. Two solutions are needed, one of silver nitrate containing

¹ Walters, H. E., Chem. News, vol. 84, 1901, p. 239; Proc. Eng. Soc. West. Pennsylvania, vol. 17, 1901, p. 257. Based on a suggestion of H. Marshall, Chem. News, vol. 83, 1901, p. 73.

2 grams of the salt to the liter, and one of manganous sulphate or nitrate containing the equivalent of 2 mg. of MnO in 10 cm.³. This last can be made conveniently by acidifying a standard permanganate solution, reducing it by sulphurous acid, and diluting appropriately. A solution of permanganate can be used directly as a color standard when very small quantities of manganese are in question. Ammonium persulphate in the solid form is also needed. The commercial article needs no purification ordinarily in this case.¹

The rock solution must be strongly acid with nitric or sulphuric acid and considerably less than 100 cm.³ in bulk unless the manganese exceeds 1 milligram in weight. To it is added 10 cm.³ of the silver solution for every milligram of metallic manganese, and it is transferred to a graduated flask of size suited to the solution. Should it show a turbidity from precipitated silver chloride, the liquid must be agitated and then filtered into the flask. About 1 gram of solid ammonium persulphate is now added and the flask is placed on the steam bath or hot plate. Very soon the pink color of permanganic acid begins to appear and increases rapidly to a maximum. The flask may be removed soon after the color begins to show and placed in cold water when it is fully developed. If the depth of color is very great the solution must be poured into a larger flask. The flask is filled with water to the mark and the contents are thoroughly mixed.

According to the depth of color there is now placed in another flask of 100 cm.³ or less volume 10 cm.³, or some multiple of that amount, of the manganese solution, so that when both solutions are oxidized and the flasks filled the color in the standard shall be more intense than in the test solution. This solution is oxidized by the aid of silver salt and persulphate in the same manner as the other, cooled, filled to the mark, shaken, and poured into a burette. Ten cm.³ is drawn off into one of the comparator cylinders shown in figure 5 (p. 36), and diluted with water from a burette till the color equals that of the properly diluted and mixed test solution, a part or all of which has been poured into the companion cylinder. The observations are made exactly as given on page 37. If the form of colorimeter depicted in figures 6 or 7 is used, the dilution of the standard solution is, of course, unnecessary. Nessler cylinders can be used instead of either of the colorimeters described. The results are very exact.

Should, perchance, a brown precipitate form during the oxidation of the standard, it will sometimes be necessary to start with a fresh portion, but often the error can be remedied by immediate addition of more silver salt and continued heating. If this treatment fails with the test solution, the precipitate must be brought into solution by a little sulphurous acid, more silver salt added, and the oxidation repeated with persulphate.

¹ See footnote, p. 112.

G. Bertrand¹ operates in nitric acid solution, employs potassium instead of ammonium persulphate, and boils the solution to destroy an excess of the persulphate. The function of the nitric acid, according to Bertrand, is not only to cause any precipitate of silver peroxide that may form to disappear on boiling, but also to assure complete transformation of the manganese to permanganate.

If the rock carries much iron, it will be well to eliminate the effect of the color of the iron by adding to the standard ferric sulphate or nitrate in proper proportion. (See p. 160.)

In order to overcome the disturbing effect of chromium, if present, M. Dittrich² precipitates all the iron and manganese by ammonia after oxidizing with persulphate, filters, redissolves the precipitate in sulphuric acid with the aid of sulphurous acid or hydrogen peroxide, warms to expel or destroy the excess of either of these, and repeats the oxidation with persulphate and silver nitrate.

D. DIRECT TITRATION OF MANGANESE.

F. J. Metzger and L. E. Marrs³ have developed a method for the direct titration of manganese in the presence of other bases, which they say is applicable to irons, steels, ores, and slags. It is based on the fact that under favorable conditions Mn^{VII} in hydrofluoric acid solution oxidizes Mn^{II} to Mn^{III} and is itself reduced to Mn^{III} . (See 21. D. b. α , p. 197.) The authors say that if sufficient of this acid is present the reaction is quantitative.

My experience with the method as the authors apply it to rocks does not bear out their claims for great accuracy, perhaps because of the disturbing influence at the end of the titration of the brown color of the manganic salt. Nevertheless, in view of the very positive statements made by Metzger and Marrs, their procedure for rocks is given below.⁴

Boil the sample (5 to 10 grams) with 5 to 15 cm.³ of dilute sulphuric acid (1:2); add 5 to 15 cm.³ of hydrofluoric acid, and boil further until the sample is completely decomposed. Add 5 to 10 cm.³ of dilute nitric acid (1:1) and 2 or 3 cm.³ of concentrated sulphuric acid. Remove from the flame and add about 1 gram of ammonium persulphate in small portions. When evolution of gas has ceased, evaporate until white fumes are evolved, cool, add 50 cm.³ of water, boil, and cool again. Transfer to a wax beaker (a ceresin bottle with the top cut off), add 5 grams of ammonium fluoride and 25 cm.³ of

¹ Ann. chim. appl., vol. 16, 1911, p. 283.

² Zeitschr. anorg. Chemie, vol. 89, 1913, p. 171.

³ Jour. Ind. Eng. Chemistry, vol. 5, 1913, p. 125.

⁴ E. Müller and P. Koppe (Zeitschr. anorg. Chemie, vol. 63, 1911, p. 160) were the originators of the method but rejected the reaction for quantitative use because of the disturbing color due to the manganic fluoride.

hydrofluoric acid (making a total volume of about 100 cm.³), and titrate to a permanent pink color with permanganate (about N/30). The value of the permanganate in terms of iron multiplied by 0.7868 gives the value in terms of manganese, or by 1.016 in terms of MnO.

12. CALCIUM AND STRONTIUM (BARIUM).

A. SEPARATION FROM MAGNESIUM.

a. GENERAL CONSIDERATIONS.

Calcium is found in rocks and minerals almost always associated with magnesium. If, as is usual, there is no excessive disparity in the proportions of the two, the oxalate method of separating the calcium from the magnesium can be used directly. Even then, apparently correct results are due to slight compensating errors. The method is less applicable if either metal preponderates very largely over the other. When magnesium preponderates greatly the calcium is incompletely precipitated if ammonium oxalate is not used in great excess, and on the other hand there is coprecipitation of magnesium oxalate if a great excess of the precipitant is used. If calcium is the greatly preponderating metal, much of the little magnesium present is precipitated with it, and the error is not overcome wholly by re-solution and reprecipitation. These are but special illustrations of the too little observed rule that in general "when testing for minute amounts of impurity, the procedure of first removing the main element by precipitation should never be followed."¹ The rule is not always applicable, but in most cases it is good practice to concentrate the minor component of a mixture in a precipitate that carries but a fraction of the major component, and upon this precipitate to apply the methods of separation that serve when the relative amounts are not altogether disproportionate. Fortunately, most silicate rocks fall in the latter category.

Strontium precipitates with the calcium in the oxalate method.² For the behavior of barium see C, page 145.

In the separation of calcium from magnesium by the ammonium oxalate method at least two precipitations are essential to the attainment of correct results, not only for complete removal of magnesium but of sodium as well, the retention of compounds of the latter element being now well known. This subject has been studied by many authors and especially by T. W. Richards, C. T. McCaffrey, and H. Bisbee,³ who call attention also to the danger of too long washing

¹ Hostetter, J. C., Jour. Ind. Eng. Chemistry, vol. 6, 1914, p. 392; Chem. News, vol. 110, 1914, p. 155.

² Confirmed by C. A. Peters, Am. Jour. Sci., 4th ser., vol. 12, 1901, p. 216.

³ Proc. Am. Acad. Arts and Sci. vol. 36, 1901, p. 375; Zeitschr. anorg. Chemie, vol. 28, 1901, p. 71.

with hot water, because of the very appreciable solubility of calcium oxalate in it. This is a point that needs greater attention than it receives from analysts. A liter of nearly boiling water dissolves over 1 cg. of calcium oxalate; at room temperatures about 7 mg. is dissolved.

b. SEPARATION WHEN NEITHER CALCIUM NOR MAGNESIUM PREPONDERATES EXCESSIVELY.

The platinum derived from the dish in the silica evaporation, except for the small portion precipitated with the manganese sulphide, is now wholly in the filtrate from the latter (11. B. a. β , p. 135). Its separation at this or any other stage is quite unnecessary; nor is the removal of ammonium chloride usually demanded, for as a rule there is no undue amount present, the first precipitation of alumina, etc., having been effected by ammonium or sodium acetate.² Therefore, without destroying ammonium sulphide the calcium and strontium are thrown out by ammonium oxalate at boiling heat, the precipitate, often darkened by deposited platinum sulphide, is ignited and dissolved in hydrochloric acid, the solution is boiled with ammonia to throw out traces of alumina sometimes present, filtered, and the calcium and strontium are reprecipitated as before, but in a small bulk of solution. For the treatment of the filtrates see section 13, Magnesium (p. 148).

For this second precipitation, and whenever a separation as complete as possible is called for by one precipitation, the following procedure of Richards and his coworkers is recommended.

The magnesium must not be in greater concentration than 1/50 normal. Add to the solution about 10 times the equivalent of ammonium chloride and enough oxalic acid to combine with all the calcium. It is advisable to repress the dissociation of the oxalic acid in advance by addition of three to four times its equivalent of hydrochloric acid. Add at intervals to the boiling solution, colored by a drop of methyl orange, very dilute ammonia, with continuous stirring, until the neutral point is just passed. Half an hour is needed to complete this operation. Then add a great excess of ammonium oxalate and let the liquid stand for about four hours. Longer standing results in reprecipitation of magnesium oxalate upon the calcium salt; with less time precipitation of the calcium is incomplete. Wash with water containing a little ammonium oxalate, in which calcium oxalate is much less soluble than in pure water. "The filtrate contains all the magnesium except 0.1 to 0.2 per cent, and in the precipitate is all the calcium with about the same deficit." This quotation refers to a first precipitation.

² If two or three precipitations by ammonia alone are depended on, the second and third filtrates are evaporated rapidly to dryness and the ammonium salts removed by ignition.

C. IGNITION OF THE CALCIUM OXALATE.

The moist precipitate of calcium and strontium oxalates, wrapped in the filter paper, is placed in a platinum crucible and heated so as to char without inflaming the paper. When the carbon has been made to disappear by stronger heat, the crucible is to be covered and blasted with an inclined flame. It is a very mistaken idea that with a really good blast it takes long to reach constant weight. Five minutes is ample, ordinarily, for any amount of lime that is likely to be met with. For ordinary amounts the heat of a large and good Bunsen burner is in reality sufficient. I was able by it in 50 minutes to reduce 3 grams of calcium carbonate to the oxide, or so nearly so that the blast afterwards caused a further loss of only 1 mg. This, of course, was with the crucible covered. The lime should not be left over half an hour in the desiccator before weighing, for it gains weight appreciably if left long.

The weighed oxide is transferred to a small flask of 20 cm. capacity, dissolved in nitric acid, and evaporated to dryness at 150° to 160°, and the separation of strontium from calcium is effected by ether-alcohol¹ as described below, under B.

The weight of the strontia found, deducted from that of the two oxides, gives that of the lime.

D. SEPARATION OF LITTLE CALCIUM FROM MUCH MAGNESIUM.

α. Preliminary remarks.—The procedure given on page 141 is applicable to almost all silicate rocks, but the results are affected by slight compensating errors, as already pointed out under A. *a*, even when the separation is made under the most carefully regulated conditions. If an extremely accurate determination of very little calcium in presence of much magnesium is desired, as in the mineral magnesite, recourse must be had to successive precipitation of the calcium, first as sulphate, then as oxalate.² Various procedures have been proposed, of which perhaps the best review is that by O. Kallauner and I. Preller.³ They found that direct weighing of the calcium precipitated as sulphate is quite unsatisfactory, but that very good results are obtainable by their modification of the sulphate

¹ See Fresenius, R., *Zeitschr. anal. Chemie*, vol. 32, 1893, pp. 189, 312, for the latest improvements in this method, in their application to considerable quantities.

² It is probable that a very good procedure would be to precipitate the calcium and magnesium together as phosphate according to 13. A. *b*. and *β* (pp. 149–150), and to determine the calcium in the ignited magnesium pyrophosphate according to 13. C. *b*. (p. 152). For this suggestion I am indebted to Dr. James A. Holladay, chief chemist of the Electro-Metallurgical Co., Niagara Falls.

³ *Chem. Zeitung*, vol. 36, 1912, p. 462. A method by A. Cappel (*Kali*, vol. 4, 1910, p. 77) is based on the precipitation of calcium by sodium bicarbonate in presence of ammonium chloride. E. C. Carron (*Ann. chim. appl.*, vol. 17, 1912, p. 127) bases a method unsupported by analytical data on the precipitation of calcium as sulphite.

method of C. Stolberg and that of E. Murmann, followed by precipitation as the oxalate.

β. *Modified Stolberg method.*—The original Stolberg method¹ begins with evaporation of a mixture of the chlorides with sulphuric acid and complete expulsion of the excess of the acid. The residual sulphates are treated with a very little water, so as to form a saturated solution of magnesium sulphate, to which is added a mixture of 10 per cent ethyl alcohol and 90 per cent methyl alcohol, in which magnesium sulphate is freely soluble. The wholly insoluble calcium sulphate is washed with a mixture of the two alcohols in the proportion 5 to 95.² The alcohols must be free from basic organic substances, which would precipitate magnesium. G. E. F. Lundell found these in one lot of methyl alcohol.

In order to shorten the operation Kallauner and Preller treat a mixture of the dry chlorides with the 10-90 alcohol mixture saturated with lithium sulphate (which is readily soluble in the alcohol), or they evaporate to dryness a solution of the chlorides with lithium sulphate, extract the residue with the alcohol mixture, and proceed in either case according to Stolberg until the sulphate is washed. They dissolve it then in hydrochloric acid and purify it by precipitation with ammonium oxalate. Needless to say, this latter operation should be done in a small volume of liquid.

γ. *Murmann's method.*³—E. Murmann's method presupposes knowledge of the amount of calcium present and is limited accordingly.

Add to the chloride solution the requisite amount of sulphuric acid to combine with the calcium, evaporate to dryness, digest and wash with ethyl alcohol (90 per cent), dissolve the precipitate in hydrochloric acid, and separate the calcium as oxalate from the contaminating magnesium salt.

δ. *Author's method.*—Tests made for me by G. E. F. Lundell, in order to learn if the separation is really complete in presence of free sulphuric acid, as recommended by me in the past (see 13. C. b, p. 152), show that with 100 mg. MgO and 1 mg. CaO the precipitation of calcium is complete by using a mixture of ethyl alcohol, water, and sulphuric acid in the proportion of 90 to 9 to 1 by volume, or one of methyl alcohol, ethyl alcohol, and sulphuric acid in the proportion of 90 to 10 to 1. With 1,000 mg. MgO and 1 mg. CaO the precipitation of calcium was not complete.

¹ Zeitschr. angew. Chemie, vol. 17, 1903, p. 741.

² Stolberg found that precipitation of magnesium sulphate from a half-saturated solution by ethyl alcohol ceases only when the alcohol is diluted with at least 40 per cent of water, and that calcium sulphate is somewhat soluble in alcohol of 90 per cent strength; hence, that direct separation seems impossible. But a saturated solution of magnesium sulphate is not precipitated by methyl alcohol.

³ Zeitschr. anal. Chemie, vol. 49, 1910, p. 688.

C. SEPARATION OF LITTLE MAGNESIUM FROM MUCH CALCIUM.

J. C. Hostetter¹ draws attention to gross errors current in the determination of very little magnesium in presence of much calcium, especially in commercial salts of calcium used as reagents, and proposes the following procedure, which, however, is not applicable for determining calcium in the same solution:

Ten grams of the calcium salt are brought into solution in water, and the solution is made up to 100 cm.³. If acid is used to bring the salt into solution, the excess is neutralized with sodium hydroxide, after the expulsion of CO₂, SO₂, etc., by boiling. The calcium oxide made from 0.3 to 0.4 gram of calcium carbonate by ignition is now added and the solution heated to boiling; the precipitate is filtered off but not washed. The precipitate is dissolved in hydrochloric acid and the calcium removed by two precipitations with ammonium oxalate. The filtrates from these two precipitates are combined, and the magnesium in the combined filtrate is determined by precipitation as ammonium-magnesium phosphate by microcosmic salt.

B. SEPARATION OF STRONTIUM (BARIUM) FROM CALCIUM.

a. BY ETHER-ALCOHOL.

The thoroughly dried nitrates obtained in A. c are treated with as little (seldom over 2 cm.³) of a mixture in equal parts of absolute alcohol and ether as may be needed to dissolve the calcium salt, solution being hastened by occasional gentle agitation. After standing overnight in the corked flask the insoluble matter is collected on the smallest possible filter and washed with more of the above mixture of alcohol and ether. After drying, a few cubic centimeters of hot water is passed through the filter, on which may remain a few tenths of a milligram of residue, which does not usually contain any lime or other alkaline earth and whose weight is therefore to be deducted from that of the lime, unless it can be shown that it is derived from the glass of the little flask in which the nitrates of calcium and strontium were evaporated. To the solution of strontium nitrate in a small beaker a few drops of sulphuric acid and then its volume of alcohol are added, whereby the strontium is precipitated as sulphate, in which form, after twelve hours, it is weighed and then tested spectroscopically as to freedom from calcium and barium.

b. OTHER METHODS.

Because of the slight solubility of strontium nitrate in amyl alcohol the method of Browning² does not appear to be adapted to the separation from calcium of the small amounts of strontium met with in rocks, though with barium the case is different, since its nitrate, according to Browning, is insoluble in absolute amyl alcohol.

¹ Jour. Ind. Eng. Chemistry, vol. 6, 1914, p. 392; Chem. News, vol. 110, 1914, p. 155.

² Am. Jour. Sci., 3d ser., vol. 43, 1892, pp. 50, 314.

A method which seems not to have been given rigid test as yet, for separating barium and strontium from calcium, is that of S. G. Rawson,¹ which is as follows: A nitrate solution of the metals is evaporated until the mass is quite dry. Concentrated nitric acid is added in excess, and the mixture is kept well stirred. After settling, the precipitate is collected in a Munroe crucible (platinum felted) and washed with more of the concentrated acid. Calcium is determined in the filtrate after evaporation. The barium and strontium nitrates are dissolved in water; the barium is determined as chromate, the strontium as sulphate in the filtrate from the barium chromate.

C. BEHAVIOR OF BARIUM.

Barium, after two ammonium-oxalate precipitations, will never be found with the ignited calcium and strontium in more than spectroscopic traces, unless originally present in excess of 3 or 4 mg., and very often only when in considerable excess.² If present with them, however, it will be separated with the strontium by ether-alcohol or amyl alcohol, and these two must then be treated by the ammonium-chromate method, given below, in order to arrive at the strontium. The barium is best estimated in a separate portion.³ (See "Barium," 15, p. 170.)

D. SEPARATION OF BARIUM FROM STRONTIUM.

Profiting by the experience of R. Fresenius and others, A. Skrabal and L. Neustadl⁴ have shown in what manner alone a very nearly correct separation of barium can be made from calcium and strontium. The following solutions are requisite:

Ammonium bichromate, 100 grams to the liter.

Ammonium acetate, *a*, 300 grams, neutralized by ammonia, to the liter.

Ammonium acetate, *b*, 20 cm.³ of *a* diluted to 1 liter.

The reaction of the acetate solutions should be alkaline rather than acid.

The method for the amounts used by the authors (0.135 gram BaO as the chloride and the same of strontium) is as follows:

To the neutral or weakly acid solution is added ammonium acetate (10 cm.³ of solution *a*) in excess. The liquid is brought to boiling and while swirled about 5 cm.³ of the bichromate solution is added. After settling and cooling the clear liquid is decanted through a filter

¹ Jour. Soc. Chem. Industry, vol. 16, 1897, p. 113.

² Hillebrand, W. F., Jour. Am. Chem. Soc., vol. 16, 1894, p. 83; Chem. News, vol. 69, 1894, p. 147.

³ For the separation and estimation of barium associated with calcium and magnesium, by the action of acetylchloride in acetone upon the mixed chlorides, consult F. A. Gooch and C. N. Boynton, Am. Jour. Sci., 4th ser., vol. 31, 1911, p. 212.

⁴ Zetschr. anal. Chemie, vol. 44, 1906, p. 742.

and the precipitate washed by decantation with ammonium acetate (solution *b*) till the filtrate is no longer perceptibly colored (100 cm.³ of wash solution). The beaker is placed under the funnel, the precipitate on the paper dissolved by warm dilute nitric acid, and the paper washed. More acid is then added to dissolve the rest of the precipitate, followed by ammonia till the precipitate forming again no longer redissolves. Ammonium acetate (10 cm.³ of solution *a*) is now poured in, the liquid brought to boiling while kept in swirling motion, allowed to cool slowly, and the precipitate is washed by decantation with solution *b* of the ammonium acetate. The barium chromate is dried and weighed as such after ignition, the filter being burned separately.

The strontium may be thrown down from the combined filtrates by ammonia and ammonium carbonate, after concentration in presence of a little nitric acid, and weighed as carbonate; or the carbonate may be redissolved, precipitated by sulphuric acid and alcohol, and weighed as sulphate.

It is probable that for the small amounts encountered in rocks a single precipitation of the barium by bichromate will suffice, but this is not so when any considerable quantities are to be separated.

E. OTHER METHODS OF DETERMINING CALCIUM AFTER PRECIPITATION AS OXALATE.

a. PRELIMINARY REMARKS.

Additional methods more or less in vogue for determining the calcium after precipitation as oxalate are the volumetric method by potassium permanganate and the conversion of the oxalate into carbonate, sulphate, or fluoride. None of these is applicable in rock analysis if it is desired to determine the strontium, except the second, but apparently any one of them will afford good results if no account is to be taken of that element. The methods have not been tested in the Survey laboratory, however, though the several gravimetric methods have been compared by O. Brunck,¹ who finds that duplicates by any one of them show better agreement than by the oxide method. Brief descriptions of them are therefore given below, as well as of the volumetric method.

It is to be said, however, regarding Brunck's determination of calcium as the oxide, that no such variations as those reported by him are ever obtained in the Survey laboratory. Duplicates by that method agree as well as his by the other methods. His high and varying results by the oxide method are probably to be attributed to the employment of a vertical instead of an inclined flame. The complete conversion of the oxide to sulphate or to fluoride by treat-

¹ Zeitschr. anal. Chemie, vol. 45, 1906, p. 77.

ment with sulphuric or hydrofluoric acid is, in my opinion, based on experience with the conversion of lead chloride to sulphate, by no means easily brought about. There will always be a tendency, where an insoluble compound is at once produced by action of one of the acids in question, for some of the original compound to be protected from conversion to the salt, even after two or more evaporations with fresh portions of acid.

It is further doubtful if the loss in weight of the crucible during blast ignition of the lime is really as great as he thinks. It is well known that barium oxide attacks platinum strongly when heated in contact with it, and it is certain that lime does so to a less but appreciable extent. That it does can be demonstrated readily by dissolving in hydrochloric acid lime that has been blasted in platinum for half an hour and precipitating and weighing the dissolved platinum. The amount recovered will nearly and sometimes quite equal the loss in weight of the crucible itself.

b. VOLUMETRIC METHOD.

The washed oxalate is rinsed into a beaker and the filter is extracted with hot dilute sulphuric acid, the filtrate being caught in the beaker. It is not permissible to omit this extraction, for simple rinsing with water will not extract all of the oxalate held in the pores of the paper. More acid is added if necessary, and the contents of the beaker are digested at a moderate heat till decomposition can be considered complete. The oxalic acid is then titrated warm at about 70° with permanganate, which has been standardized against pure Iceland spar dissolved in hydrochloric acid and precipitated as the oxalate, or, better, against the Bureau of Standards' sodium oxalate.

c. BY WEIGHING AS THE CARBONATE.

The oxalate is ignited gently to convert it to carbonate and is then digested with a few drops of a solution of ammonium carbonate. The liquid is evaporated cautiously and the residue ignited gently to just visible dull redness and weighed. The treatment with ammonium carbonate, etc., is repeated till constant weight is reached.

d. BY WEIGHING AS THE SULPHATE.

The strongly ignited oxide is slaked cautiously with water and a slight excess of sulphuric acid is added. The liquid is concentrated by evaporation and the excess of acid removed in the radiator (fig. 2, p. 33). The dry sulphate is then ignited moderately (to dull redness for a short time) and weighed, the treatment with acid, etc., being repeated to constant weight.

e. BY WEIGHING AS THE FLUORIDE.

The strongly ignited oxide is slaked with water and covered with hydrofluoric acid, the excess of which is removed on the bath and the residue ignited for a few moments and weighed. The treatment with acid, etc., is to be repeated till the weight becomes constant. According to Brunck this last method is simpler than the carbonate or sulphate method, and in the hands of the inexperienced leads to better results, though he regards the sulphate method as the best in experienced hands.

13. MAGNESIUM.

A. PRECIPITATION.

a. CONDITIONS NECESSARY FOR THE PRODUCTION OF A NORMAL PRECIPITATE.

There are few analytical procedures regarding which so much uncertainty has existed and still exists as that by which magnesium is precipitated as the ammonio-phosphate, notwithstanding the enormous mass of detailed work that has been done on the subject. The work of H. Neubauer,¹ confirmed in part and supplemented by F. A. Gooch and Martha Austin,² seemed to clear the ground fairly well. Neubauer found that precipitation is complete even in the presence of large quantities of salts of ammonium, including the oxalate, but that the composition of the precipitate is largely affected by ammonium salts and also by the way in which the precipitation is made. The precipitate is also said to be rendered impure if sodium chloride is in the solution. Hence the need for a double precipitation. Gooch and Austin show that the large amount of ammonia of 0.96 specific gravity (one-third the original volume of the solution) usually prescribed is not only unnecessary, but, in fact, disadvantageous, at least until the precipitate has fully formed. The authors named agree that it is only by working under certain conditions—absence of any large excess of precipitant, of ammoniacal salts, and of ammonia—that a precipitate of normal composition is obtainable (see below). From their labors it would seem clear that the common way of adding the phosphate precipitant to the ammoniacal solution of the magnesium salt is not calculated to produce a precipitate of normal composition. The precipitant should be added to the acid solution of the magnesium, and ammonia should then be added in slight excess.

The precipitate as ordinarily formed contains an excess of phosphorus, a condition which Neubauer ascribed to admixture of perhaps $\text{Mg}(\text{NH}_4)_4(\text{PO}_4)_2$, the result being that when it is ignited in the ordinary way the calculated value for magnesium will be high, because of the formation of some metaphosphate. K. Bube,³ however,

¹ Zeitschr. angew. Chemie, 1896, p. 435.

² Am. Jour. Sci., 4th ser., vol. 7, 1899, p. 187; Chem. News, vol. 79, 1899, pp. 233, 244, and 255; Zeitschr. anorg. Chemie, vol. 20, 1899, p. 121.

³ Zeitschr. anal. Chemie, vol. 49, 1910, p. 587.

seems to have shown that the normal precipitate carries with it ammonium phosphate. In order to overcome the resulting error Neubauer considered it to be absolutely necessary to blast the precipitate for half an hour, and after weighing to repeat the blasting for a second half hour. If the weight has not changed the phosphate is then entirely pyrophosphate, which is quite unaffected by further blasting. (See, however, B, p. 150.) The intense heat has volatilized the ammonium phosphate or has caused a decomposition of the metaphosphate with volatilization of P_2O_5 , as follows: $2 Mg(PO_3)_2 = Mg_2P_2O_7 + P_2O_5$. Neubauer worked with the usual excess of ammonia added after the bulk of the precipitate had formed, and it remains to be seen whether by precipitating and working according to Gooch and Austin the composition of the precipitate is always close enough to the ideal $MgNH_4PO_4$ to obviate the necessity for blasting.

Gooch and Austin call attention to a modification proposed long since by Wolcott Gibbs,¹ whereby the phosphorus and magnesium salts are first boiled together in neutral solution for a few minutes and to the cooled solution ammonia is added. The results are said to be remarkably exact, but K. K. Järvinen² reports to the contrary. Järvinen and numerous other chemists have published papers upon one phase or another of the general subject, and many are the modifications of procedure that have been proposed. They need not be discussed here, for most of them aim at obtaining a precipitate of normal or nearly normal composition by making only a single precipitation, whereas a repetition is called for in mineral and rock analysis, and the proposed procedures do not adapt themselves thereto well, if at all. Mention may be made, however, of the latest contributions—numerous papers by D. Balarew³ and one by Z. Karaoglanow and P. Dimitrow.⁴ These authors discuss also the conditions under which the glowing of magnesium-ammonium phosphate occurs when it is being converted to pyrophosphate by ignition, the probable causes of the phenomenon and ways of inhibiting it, and the means of whitening magnesium pyrophosphate that becomes discolored during ignition.

D. PRECIPITATION AND FILTRATION.

a. First precipitation.—The first precipitation is made without precautions in the ammoniacal filtrate from the first calcium-oxalate separation (12. A. b, p. 141) by sodium-hydrogen phosphate⁵ (microcosmic salt in indefinite decided excess and with addition of about one-fifth the volume of strong ammonia solution at the end. Vigor-

¹ Am. Jour. Sci., 3d ser., vol. 5, 1873, p. 114.

² Zeitschr. anal. Chemie, vol. 44, 1905, p. 335.

³ Zeitschr. anorg. allg. Chemie, vols. 101–104, 1918–1919.

⁴ Zeitschr. anal. Chemie, vol. 57, 1918, p. 353.

⁵ The objection that has been made by one writer to the use of this salt instead of disodium-hydrogen phosphate is, so far as my experience teaches, entirely groundless.

ous stirring hastens formation of the precipitate. It is not necessary first to remove ammoniacal salts unless very little magnesium is present, and then only in order to hasten precipitation. The facts that large quantities of these salts retard precipitation and that the composition of the precipitate is affected by them as well as by the way in which the precipitation is made are of importance only when a single precipitation is to be made or in the final of two or more.

Continued agitation of the liquid by a mechanical stirrer is of advantage in greatly shortening the time of complete precipitation, which is in general shorter the greater the quantity of magnesium present.

After standing for at least 4 hours, and for as much as 12 hours if the precipitate was slow to form, filter through paper. Wash with water to which about one-tenth its volume of strong ammonia water has been added. Half a dozen washings suffice after the rinsings from the dish have passed the filter. Filtering and washing are done best without much if any suction, but it is well to suck the precipitate dry at the end.

β. *Second precipitation.*—Platinum sulphide usually strongly contaminates the separated phosphate, but this matters not, as it remains on the filter when the phosphate is redissolved in hydrochloric acid, of which not more than the amount really needed should be used. The stirrer must be treated with acid; also, the beaker or dish. The solution thus obtained is united with that of the residue from evaporation and ignition of the second filtrate from the calcium oxalate (12. A. b, p. 141) and is diluted if necessary. A few drops of sodium-ammonium-phosphate solution are now added, and ammonia, drop by drop, with constant stirring till in slight excess and the crystalline precipitate has formed well. Once formed, a few cubic centimeters more of ammonia is to be added.

The filtering and washing are done on a fresh paper after three to six hours, and great care must be exercised to clean the precipitation vessel and the stirrer thoroughly from strongly adhering precipitate by the aid of a "policeman" or feather.

Were it not for the necessity of examining the precipitate for impurities after ignition (C, p. 152) a Gooch filtering crucible could be used with advantage instead of a paper filter, provided the asbestos felt is well constructed and not of the serpentine variety. A Munroe (platinum felted) crucible may be used, but subsequent operations are shortened if paper is employed.

B. IGNITION OF THE PRECIPITATE.

The precipitate, wrapped in its moist paper, is dried in a weighed platinum crucible, the paper then slowly charred without allowing it to ignite, the carbon burned off over a gradually increasing flame,

and finally a weak blast applied for a long time in order to insure volatilization of any excess of P_2O_5 over and above that required for the pyrophosphate formula. (See A. a, p. 148.) After weighing, the heating is repeated as often as may be necessary to bring the phosphate to a constant weight.

The danger of attack of the platinum crucible by igniting the precipitate in contact with the paper is very slight, though it has happened once or twice in my experience that a crucible has been ruined by so doing. Why reduction should have occurred in these cases and not in the hundreds of others is not known.

The experience of the Survey chemists was for a time decidedly adverse to the blasting of magnesium pyrophosphate as prescribed by Neubauer, whether obtained by precipitation of magnesium or of phosphate solutions. If the weights were not large the salt fused in part or wholly, and when this occurred reduction seemed to be rapid and the crucible was rather strongly attacked, as shown by its loss in weight after dissolving out the pyrophosphate. Presumably this effect was caused by a blast of higher temperature than that employed by Neubauer, who is very emphatic in his assertion that neither pure pyrophosphate nor crucible suffers the slightest loss when blasted for hours. This seems to be true with a blast of but moderate temperature, giving less than $1,100^\circ$ in the crucible. What effect the presence of slight amounts of foreign phosphates may have in increasing the fusibility of magnesium pyrophosphate is unknown. Järvinen found that his precipitates obtained by the Gibbs method fused readily and gave too high results, and further that P_2O_5 did seem to volatilize slowly from $Mg_2P_2O_7$ over the blast.

The practice of Fresenius and others of moistening the ignited pyrophosphate with a drop or two of nitric acid, evaporating, and again igniting, in order to insure obtaining a perfectly white precipitate, is open to objection. Chemical changes occur which invite loss during the final ignition.¹

Still more objectionable is the procedure recommended by several authors, to dissolve the precipitate of magnesium-ammonium phosphate in nitric acid, to evaporate the solution in a platinum crucible and then to ignite carefully. The objections are that the effect of the nitric acid is far more pronounced than when the pyrophosphate is treated with a drop or two of nitric acid, and the final result is not pure pyrophosphate but a mixture of phosphates, one of which is probably a metaphosphate, as it is insoluble, or nearly so, in hydrochloric and nitric acid. However, the procedure affords a most deli-

¹ Campbell, D., Phil. Mag., vol. 24, 1862, p. 380. Luck, E., Zeitschr. anal. Chemie, vol. 13, 1874, p. 225. Karaoglanow, Z., and Dimitrow, P., Zeitschr. anal. Chemie, vol. 57, 1918, p. 353.



cate test for contamination by manganese, for if it is present a pink color of varying intensity, according to the amount, becomes apparent as the mass approaches dryness.

C. CONTAMINATION BY AND REMOVAL OF BARIUM, CALCIUM, AND MANGANESE.

a. BARIUM.

Barium phosphate will not contaminate the second magnesian precipitate unless there are notable amounts of barium in the rock, in which case it must be removed by sulphuric acid prior to the final precipitation of the magnesium.

b. CALCIUM.

Calcium, however, is probably never absent, and must be determined and allowed for as follows:

α. Preferred method.—The ignited pyrophosphate is dissolved in a little dilute sulphuric acid and enough absolute alcohol is added to make about 90 to 95 per cent of the final volume. After several hours the sometimes almost invisible precipitate of calcium sulphate is brought onto a small filter and washed free of phosphoric acid with alcohol, dried, and dissolved in hot water slightly acidulated with hydrochloric acid. After rendering the solution ammoniacal and heating, a few crystals of ammonium oxalate are thrown in and the heating is continued till a precipitate becomes visible. In a short time it may be filtered, ignited, and weighed as calcium oxide. Its weight, averaging less than 0.5 mg., is to be added to that of the lime already found and subtracted as tricalcium phosphate (not pyrophosphate) from that of the magnesium pyrophosphate, in order to arrive at a truer figure for magnesia. The alcoholic filtrate is to be evaporated, ignited to destroy organic matter, and tested for manganese, as under c below.

G. E. F. Lundell has shown (see 12. A. d. 8, p. 143) that this separation is satisfactory with amounts of 100 mg. of MgO and 1 mg. of CaO, but that it is incomplete with 1,000 mg. of MgO and 1 mg. of CaO.

β. Alternative method.—A less certain way to separate the calcium that is in the pyrophosphate, but one which admits of detecting small amounts of aluminum and iron that may have escaped precipitation earlier in the analysis, is the following:

To the ignited pyrophosphate dissolved in but slight excess of hydrochloric acid is added ammonia to alkalinity, and then acetic acid, drop by drop, till the solution, which should measure 10 to 30 cm.³ and not be hot, clears. It happens now and then that a little flocculent matter fails to dissolve. This is to be removed, ignited,

and subtracted from the original weight if proved to be free from magnesium, which it often contains. (See c, below.) It is likely to consist in great part or wholly of phosphates of aluminum, iron, or manganese, and shows often a reddish color on ignition. If an excess of acetic acid has been added, most of this is cautiously removed by ammonia. Then a drop or two of solution of ammonium oxalate is added, and the small beaker is set aside for 12 hours if necessary. Almost invariably a small precipitate shows itself, which, if fine grained and nonadherent to the glass, may be regarded as pure calcium oxalate; otherwise it contains or may consist largely of magnesium oxalate. In that case it is to be collected, ignited, redissolved, and reprecipitated. This separation, to be satisfactory, requires great care.

C. MANGANESE.

A separation from one another of the iron, aluminum, and manganese which the flocculent precipitate mentioned under the second method in b may contain is not worth the trouble, careful prior treatment being presupposed. The first two constituents named may have been introduced since the original precipitation of the iron and aluminum, and their amount in terms of those elements is very small. But the amount of manganese it contains may be a sensible proportion of the whole of that element if bromine or ammonium persulphate was not used to secure its removal earlier in the analysis. The precipitate should therefore be brought into nitric or sulphuric acid solution. The solution containing the magnesium is also manganiferous. It is to be evaporated to dryness, the volatile salts expelled by ignition, and the residue again evaporated two or three times with a few drops of nitric acid, or once with sulphuric acid, to certainly remove all traces of chlorine, and united with the small solution above mentioned. The manganese is now determined colorimetrically, as in 11. C. b (p. 137), and its amount added to that already found, unless the total has been ascertained from a separate portion of the sample. In any case its amount, if significant, is to be deducted as pyrophosphate from the gross weight of the magnesium pyrophosphate.

The distribution of the manganese over the alumina, lime, and magnesia, when ammonia has been employed for the precipitation of the alumina and no attempt has been made to remove the manganese at all, is shown in the table on page 134.

D. LIABILITY TO ERROR IN THE AVERAGE MAGNESIUM DETERMINATION.

Experience has shown that most analysts are prone to make a very serious plus error in determining moderate amounts of magnesia, such as are found in limestones and Portland cements. The

causes of this error will be sufficiently apparent after a careful perusal of the foregoing pages. Everyone ought to make the tests for foreign contamination just described, if only to convince himself of the reality of the error, even after very careful work.

14. TITANIUM.

A. GENERAL CONSIDERATIONS.

Since the last edition of this work appeared the analytical study of titanium has received great attention, not so much from rock analysts as from steel-works chemists, with respect to both the ores and the metals and alloys derived from them. The same is true to a degree of zirconium. As zirconium is a very common though minor constituent of rocks and in many of its chemical characteristics patterns after titanium, no presentation of methods of precipitation and separation of the latter can be made without frequent reference to the former, particularly when gravimetric methods are considered.

The analyst will welcome suggestions as to the relative values of the methods and as to the circumstances under which one is to be preferred to another, hence a few are offered in the following paragraphs.

When titanium and zirconium are unaccompanied by other elements that would be precipitated, it is best to throw them out by ammonia. Otherwise, under favorable conditions the colorimetric method for titanium is believed to be the best and quickest for such amounts as are found in rocks. The favorable conditions referred to are absence of large amounts of iron and phosphorus, alkali salts, vanadium, and even traces of fluorine. The use of the colorimetric method when one or more of these are present in disturbing amount introduces so many complications that it is advisable to employ this method, whenever possible, only after the titanium has been separated from all interfering elements by one or another of the procedures given under 10. B, D, E (pp. 126-132). Under certain conditions, as in the absence of zirconium, it may suffice to weigh the titanium so separated, but generally the determination by color or by titration will be necessary. Which course to pursue the analyst will soon learn to decide when he has familiarized himself with the limitations and advantages of all the methods.

Of gravimetric methods, the Thornton or "cupferron" and the Baskerville methods, being much simpler than that of Gooch, seem likely to supersede it to a large extent. The interference of zirconium if present in more than traces also limits the usefulness of the Gooch method. The older method of precipitation by long boiling of a nearly neutral sulphuric solution need not be considered.

The volumetric methods have been so perfected that they may be regarded as eminently satisfactory in the absence of interfering elements. They have the great advantage of being applicable in the presence of iron and aluminum and are therefore likely to find most extended use in assaying ores and technical products.

In general it will be advisable to employ either the colorimetric or a volumetric method as the final test after separating interfering elements. The choice of a procedure will also be influenced by the purpose in view. If only the percentage of titanium is sought, a method may be acceptable which could not be introduced in a scheme for complete analysis.

The above remarks are predicated upon the assumption that it is titanium without regard to its state of oxidation that is to be determined. In almost all titaniferous minerals the element is beyond doubt in the quadrivalent state, corresponding to the oxide TiO_2 . There is some reason to believe, however, that it may here and there be in the trivalent state, corresponding to the oxide Ti_2O_3 . The proof is fraught with almost unsurmountable difficulty at present, mainly because of the general occurrence of iron. Until we know how to ascertain if the element is present in the lower state of oxidation it would be premature to try to indicate analytical means of differentiating the two states of oxidation; hence the directions that follow assume the quadrivalent state.

B. COLORIMETRIC DETERMINATION WITH HYDROGEN PEROXIDE.

a. PRINCIPLE OF THE METHOD (WELLER'S)¹ AND THE CONDITIONS THAT AFFECT IT.

The colorimetric method consists in comparing the color of a known bulk of solution to be tested with that of a standard solution of titanous sulphate, both having been fully oxidized by hydrogen peroxide. The strength of the peroxide should be approximately measured by titration with permanganate on opening a fresh bottle and again after a few weeks, otherwise very serious error may arise through its deterioration.

Mere traces of hydrofluoric acid or a fluoride in either the peroxide or the titanium solution render this method inexact by partly bleaching the yellow color,² hence care should be exercised as to the character of the peroxide, of which the commercial brands often contain fluorine. (For methods of testing see p. 46.) For the same reason the peroxide should be free from appreciable traces of phosphoric acid. (See e. γ, p. 161.) The "perhydrol" of Merck is a most excellent preparation, though some commercial brands are satisfactory.

¹ Ber. Deutsch. chem. Gesell., vol. 15, 1882, p. 2593.

² Hillebrand, W. F., Jour. Am. Chem. Soc., vol. 17, 1895, p. 718; Chem. News, vol. 72, 1895, p. 158; Bull. U. S. Geol. Survey No. 167, 1900, p. 56.

Dunnington¹ has pointed out the necessity for the presence of at least 5 per cent of sulphuric acid in solutions which are to be thus tested for titanium, in order, as he concluded, to prevent partial reversion to metatitanic acid, which does not give a color with hydrogen peroxide. P. Faber² believes that failure to get full coloration in absence of excess of acid is not due to reversion, but to the presence of a weakly coloring basic sulphate of titanium. (See, however, below as to the effect of alkali sulphates.) He showed that the normal sulphate suffers loss of acid at moderate temperatures and that even in a bisulphate fusion it becomes basic. L. Weiss and H. Kaiser³ do not accept Faber's explanation. Faber⁴ explains the bleaching effect of phosphoric acid or a phosphate as due to the slow formation of a salt of the peroxide. The color can be partly restored by adding sulphuric acid.

If iron is present in the rock or mineral to the extent of several per cent, its color affects the result. (See e, p. 160.)

In the absence of fluorine the mineral constituents that are likely to be present in important amounts in the titanium solution undergoing test do not appear to exert any appreciable effect, according to George Steiger,⁵ but H. E. Merwin⁶ maintains that alkali sulphates bleach markedly unless much sulphuric acid is present. He gives the following data:

Sulphate (grams).	Acid (cm. ³).	Bleaching (per cent).
3	0.5	15
	2.0	9
	8.0	2
6	0.4	21
	2.9	14
	8.0	5

Now, since alkali sulphates are almost always present in the test solution as ordinarily prepared (9. C. a. β , p. 120) in amounts up to or exceeding 6 grams, he concludes that all titanium determinations hitherto made by colorimetry are too low.

Merwin's statements as to the bleaching effect of alkali sulphates, both in presence and absence of fluorine, were confirmed by William Blum at the Bureau of Standards in 1909. Blum emphasizes in an unpublished memorandum the desirability of the preparation by the analyst of diagrams showing the corrections to be applied under his working conditions.

¹ Jour. Am. Chem. Soc., vol. 13, 1891, p. 210.

² Chem. Zeitung, vol. 31, 1907, p. 263.

³ Zeitschr. anorg. Chemie, vol. 65, 1910, p. 345.

⁴ Zeitschr. anal. Chemie, vol. 46, 1907, p. 277.

⁵ Jour. Am. Chem. Soc., vol. 30, 1907, p. 219.

⁶ Am. Jour. Sci., 4th ser., vol. 28, 1909, p. 119.

Merwin also found that the color intensity is increased by increase of temperature.

In spite of the above observations the colorimetric method gives results that are probably fully equal to those attainable by the best gravimetric method and in much less time, for such percentages as are found in rocks, clays, and soils, usually under 1 per cent, but occasionally rising to 2 or even 3 per cent or more. Normally the error should not exceed 2 per cent over a wide range of concentrations.¹

B. PREPARATION OF THE STANDARD.

Potassium titanium fluoride, K_2TiF_6 , serves best as the starting point for the preparation of the standard solution. A quantity of this is recrystallized from boiling water one or more times, dried, and preserved in a glass-stoppered bottle. Enough of it to make one-half to 1 liter of a standard sulphate solution containing as nearly as may be 1 gram of TiO_2 to the liter is put into a platinum dish and evaporated several times with strong sulphuric acid without bringing to dryness, till the fluorine is completely expelled. The residue is then taken up with water containing enough sulphuric acid to make at least 5 per cent of the latter when fully diluted. Two 50 to 100 cm.³ portions of the prepared solution are then further diluted, boiled, and precipitated with ammonia. The precipitates are collected on paper, washed with hot water till free from alkali, ignited moist in the filter, blasted, and weighed. Duplicates should agree almost exactly. From the averages of the weights found the strength of the solution is calculated and the result affixed to the bottle containing it. The stopper of the bottle should be coated with vaseline and the needed quantities of solution should be withdrawn by a pipette, never poured. In a solution so prepared there is not enough alkali sulphate to weaken the color when peroxidized.

In making an analysis 5 cm.³ of the standard solution (or 10 if the larger amount is needed) is mixed with a sufficiency of hydrogen peroxide (2 cm.³ of 3 per cent reagent is ample for 10 cm.³ of the standard) and diluted with 5 per cent sulphuric acid in a measuring flask to 50 or 100 cm.³, according to the original volume. Each cubic centimeter of the diluted standard will then contain nearly, if not exactly, 0.1 mg. of TiO_2 .

C. THE TEST SOLUTION.

1. Titanium can be determined most conveniently, as a rule, in the solution which has served for the titration of total iron (9. C. a. β , p. 120). The direct use of this solution involves, however, for

¹ Wells, R. C., Jour. Am. Chem. Soc., vol. 33, 1911, p. 501; Zeitschr. anorg. Chemie, vol. 70, 1911, p. 399.

accurate work corrections for its iron and alkali sulphate contents, and sometimes for vanadium, as given later. The effect of the alkali salt can be overcome by an ammonia precipitation, moderate washing of the precipitate, and its solution in 5 per cent sulphuric acid.

2. The error arising from the use of alkali sulphates can also be avoided by making the determination on some other portion of the rock powder than that indicated in the foregoing paragraph. At one time it was the practice in the Survey laboratory to combine it with the determination of barium, as described in Bulletin 148, by decomposing the powder by sulphuric and hydrofluoric acids,¹ expelling the latter by repeated evaporations with sulphuric acid, taking up with dilute sulphuric acid,² filtering from barium sulphate, etc., and estimating the titanium colorimetrically in the filtrate. The expulsion of fluorine must be thorough, or else the titanium result will be low, as already stated (p. 155), and it is not always easy to effect this complete removal, though the time required to do so seems to be in no slight degree dependent on the nature of the fluorides to be decomposed. Long after every trace of fluorine seems to be gone the formation of a crust on the evaporating solution sometimes allows an accumulation of enough hydrofluoric-acid gas to become plainly manifest to the smell on breaking the crust.³

3. Both the iron and alkali effects are excluded if the determination is made on the precipitate of TiO_2 and ZrO_2 obtained by one of the methods given under 10. B, C, D, E (pp. 126-132).

4. The residue from an alkali-carbonate fusion of rock powder, which has been obtained as in 15. A (p. 170), can be used conveniently, either before or after separation of zirconium (16. A, p. 173). Prior removal of zirconium is to be preferred for the reason that this is done in a small volume of solution and with restricted acidity, whereas the titanium is determined as a rule in a larger volume containing 5 per cent of sulphuric acid. The expulsion of most of this acid after determining the titanium, in order to bring the solution to the desired smaller volume, takes time, and to neutralize it with ammonia would produce a concentration of sulphate that might be objectionable in the subsequent precipitation of the zirconium. The conditions are such as to involve in the titanium determination a

¹ It is to be borne in mind that evaporation with hydrofluoric acid alone results in loss of titanium by volatilization, but that there is no loss if excess of sulphuric acid is also present.

² With acid rocks solution is very complete, and it can be made nearly so with the most basic by transference to a small beaker and gentle boiling. The residue thus obtained may contain, besides barium sulphate, a little calcium sulphate, zircon, andalusite, topaz, and possibly a trace of titanium in some form. It is therefore to be fused thoroughly with sodium carbonate, leached with water, fused with potassium pyrosulphate, dissolved in dilute sulphuric acid, filtered, and the filtrate added to the main one. The insoluble matter will now be chiefly barium sulphate, for the further treatment of which see 15. A, page 170.

³ See footnote on p. 90 for a procedure to facilitate the removal of fluorine.

correction for the iron of the rock, whether zirconium is first removed or not. If it is removed first, a further correction may have to be made for the alkali sulphate that results from the addition of the sodium phosphate used to precipitate the zirconium and also, possibly, for the phosphoric acid in the rock and that added. However, in most cases the amounts of sodium phosphate needed for two precipitations of the zirconium should not produce a sensible error in the value found for the titanium. The precaution should never be omitted, when determining the titanium here, to combine the two filtrates from the zirconium phosphate in order to find all the titanium.

The needs of the case or the convenience or preference of the analyst after he has acquired experience will determine which of the courses outlined in paragraphs 1-4 to pursue in determining titanium by colorimetry. Naturally, a procedure is to be preferred which will obviate the need for corrections, but in order to secure final conditions which satisfy this aim it were folly to run the risk of incurring other errors of uncertain and varying magnitude when it is possible, though perhaps troublesome, to apply corrections.

Even if no corrections are applied in rock analysis the error in the titanium value found is so small as to be of rather slight importance, especially if it is known to be always in one direction. Of course, any error incurred involves an equal and opposite one in the value found indirectly for alumina.

d. THE COLOR COMPARISON.

The sulphate solution containing the titanium, having been evaporated, if necessary, to less than 100 cm.³, is to be oxidized fully with hydrogen peroxide, and, if the color is less intense than that of the standard, is made up to 100 cm.³ with dilute sulphuric acid in a measuring flask and mixed; otherwise, in a flask of sufficient size to insure that its color shall be less intense. The mixed solution should contain at least 5 per cent of the acid. One of the rectangular glasses (fig. 5, p. 36) being filled with the solution to be tested, 10 cm.³ of the diluted standard is run into the other from a burette, and sulphuric acid of 5 per cent strength is added from a second burette until there is no distinction as to color. The temperatures of test solution and standard should be alike. A second and a third portion of the standard can be run in and diluted and the mean of several determinations struck, when a simple calculation gives the percentage of TiO_2 in the rock, the amounts in the two solutions being directly as their volumes, provided acid and interfering substances are present in each in like amounts.

If the convenient but expensive Soleil-Duboscq colorimeter is used, or the modification of Steiger or Schrener (figs. 6, 7, pp. 38, 40), or the

simple Nessler tubes, it is of course unnecessary to dilute the rock solution to the extent above required, should it be stronger than the standard. Experience has shown, however, that differences can not be estimated sharply in strongly colored solutions, and that the results are much more satisfactory when the color intensity is not much, if any, greater than that given by a diluted standard of the above concentration—that is, 0.1 mg. TiO_2 per cubic centimeter.

C. CORRECTION FOR THE COLOR OF FERRIC SULPHATE.

The error introduced by iron in consequence of the yellowish color of its sulphate solution, is practically negligible unless its percentage is high, say, over 5 per cent. Correction should be applied in one of the following ways:

α. By allowing for the coloring power of the iron in the test solution.—The color of ferric sulphate solution can not be matched closely by that of one containing titanium peroxide, but tests that have been made go to show that the coloring effect of 0.1 gram Fe_2O_3 in 100 cm.³ of 5 per cent sulphuric acid solution is about equal to 0.2 mg. of TiO_2 in 100 cm.³ when oxidized by hydrogen peroxide. This amounts to a correction of only 0.02 per cent on 1 gram of rock containing the unusual amount of 10 per cent Fe_2O_3 . The following methods are probably more exact with high iron percentages, though not so expeditious:

β. By addition of iron to the standard.—W. A. Noyes¹ adds to the standard solution approximately as much ferric iron as will give it, after the colors are matched, the same iron strength as the test solution. This could not be done with the apparatus depicted in figs. 6, 7 (pp. 38, 40), though practicable with Nessler tubes. In using the Survey colorimeter (fig. 5, p. 36) it would perhaps be best to make first an approximate determination of the titanium in order to find the final volume of the standard after dilution and then to make an exact determination, having added to a fresh portion of the standard the requisite amount of iron salt.² For all practical purposes it would probably be sufficient to add the requisite amount of iron salt in solid form to the standard after having diluted it nearly enough to match the test solution, and after it has dissolved to proceed with the test. But this procedure has the disadvantage that each comparison would necessitate the weighing out of a separate portion of iron salt, whereas by the following method the number possible would be limited only by the stock of diluted standard and of prepared ferric sulphate solution which serves for its further dilution.

¹ Jour. Anal. and Appl. Chem., vol. 5, 1891, p. 39.

² Ferric-ammonium alum is most convenient for the purpose, but its use introduces an error due to the bleaching effect of the ammonium sulphate it contains. The amount of this is, however, so small as to give rise to an error that is probably negligible.

The amount to be used per cubic centimeter of diluent is calculated as follows: Let A be the number of cubic centimeters of the test solution, a of the standard used, b of the water needed to dilute the standard in the preliminary test, p the weight of iron in terms of Fe_2O_3 in A , and x the weight of iron in terms of Fe_2O_3 to be contained in each cubic centimeter of water used for diluting the standard in the final tests. Then $x = \frac{a+b}{Ab}p$. It will of course be understood that a new test solution requires the preparation of a new iron solution with which to dilute the standard.

γ . *By the use of phosphoric acid.*—The color of a ferric sulphate solution is removed by addition of phosphoric acid. Several observers have, however, noticed that this acid greatly weakens the color of a titanium peroxide solution. This is no objection to its employment in titanium colorimetry, provided a corresponding amount is also added to the standard that serves for comparison. It can be used as the acid or in form of an alkali salt.

A known amount, sufficient to decolorize the iron, is first added to the test solution before complete dilution, and the amount to be contained in each cubic centimeter of the water used in the final dilution of the standard can be found like the iron in β above.

Both P. Faber,¹ in the paper already cited on page 156, and J. H. Walton, jr.,² have experimented with the method and report excellent results. Walton gives data showing the effect of increasing amounts of phosphoric acid in bleaching the titanium color, from which and from corroborative tests made in the Geological Survey laboratory it appears that with highly phosphatic minerals and ores their phosphorus content must be taken into account. The percentages of phosphorus in rocks are too small, even in extreme cases, to affect the color of the titanium that may be present when peroxidized.

f. CORRECTION FOR THE EFFECT OF ALKALI SULPHATES.

In order to correct for the bleaching effect of alkali salts, the standard may be diluted with alkali sulphate solution in the same manner as with ferric iron or phosphoric acid in e , β and γ ; or Merwin's corrections³ may be applied. These vary with the amounts of titanium in the solution, but

in rock analysis, by using 6 grams of pyrosulphate, which is equivalent to 4 grams of normal sulphate, and 2 grams of acid for the melt containing the titanium, and dissolving this in water to which 10 cm.³ of strong sulphuric acid has been added, a nearly negligible correction of only 3 per cent need be

¹ Chem. Zeitung, vol. 31, 1907, p. 263.

² Jour. Am. Chem. Soc., vol. 29, 1907, p. 481.

³ Am. Jour. Sci. 4th ser., vol. 28, 1909, p. 119.

added. If the titanium exceeds 0.02 gram, no correction is required. In case the melt is dissolved in 100 cm.³ of 5 per cent sulphuric acid, the titanium found—if the amount is between 0.002 gram and 0.01 gram—is too low by approximately 0.0004 gram.

g. CORRECTION FOR THE EFFECT OF VANADIUM.

As vanadium in acid solution gives a color with hydrogen peroxide, a correction for it may have to be made sometimes. It is, however, improbable that the amounts of vanadium occurring in rocks are ever sufficient to influence in a disturbing degree the color due to the titanium. Should the unexpected case present itself, the best procedure would seem to be to precipitate the titanous oxide (alone or mixed with other oxides) to fuse with sodium carbonate, and, after extracting with water and filtering, to make the color determination on the residue brought into sulphuric acid solution.

J. W. Mellor, however, has devised a procedure for the colorimetric determination of titanium in the presence of vanadium. The method requires great care and is vitiated by the presence of more than traces of iron; hence, as occasion to use it will seldom arise, it will suffice to refer to the sources of information that are given in the footnote.¹

C. GRAVIMETRIC METHODS.

a. GOOCH'S METHOD.

α. *Description of the method.*—When titanium is present in excess of 4 to 5 per cent and whenever for any reason it is desired to employ a gravimetric method, that of F. A. Gooch² was for quite a time unequalled, provided zirconium is absent. It is applicable to any solution of the rock which is free from silica, and consequently to the mixture of oxides obtained according to the main procedures described in section 8. With one or two minor modifications introduced by T. M. Chatard³ it is as follows:

After removing iron as sulphide (9. E, p. 124) the ammonium tartrate is to be destroyed, preferably by Thornton's procedure given under 10. B (p. 126), or as follows, according to Gooch:

Potassium permanganate to the extent of two and one-half times the weight of the tartaric acid used is made into a strong solution, and to the ammoniacal filtrate from the iron sulphide enough sulphuric acid is introduced to leave some excess after all the permanganate has been reduced. After expulsion of hydrogen sulphide by

¹ Trans. English Ceramic Soc., vol. 12, 1912-1913, p. 33. Mellor, J. W., Quantitative inorganic analysis, p. 486; Clay and pottery industries, vol. 1, 1914, p. 325.

² Proc. Am. Acad. Arts and Sci., new ser., vol. 12, 1885, p. 435; Bull. U. S. Geol. Survey No. 27, 1886, p. 16; Chem. News, vol. 52, 1885, pp. 55, 68.

³ Am. Chem. Jour., vol. 13, 1891, p. 106; Bull. U. S. Geol. Survey No. 78, 1891, p. 87; Chem. News, vol. 63, 1891, p. 267.

boiling, the permanganate is added gradually to the hot solution contained in a large beaker or flask. A vigorous reaction ensues. When a permanent brown precipitate of manganic hydrate appears, the tartaric acid has been fully broken up, and the precipitated manganese is to be redissolved by a few drops of ammonium bisulphite or of sulphurous acid solution.

Ammonia is then added in slight excess, followed at once by acetic acid in considerable excess, and the boiling is continued for a few minutes. Thereby the titanium is freed from most of the alumina, and from lime and magnesia if they had not been removed earlier, also from most of the manganese introduced. The precipitate is filtered and washed with water containing acetic and sulphurous acids, then ignited, fused thoroughly with sodium carbonate,¹ and leached with water to remove phosphoric acid and most of the remaining alumina. The residue is again ignited and fused with sodium carbonate. To the cooled melt in the crucible strong sulphuric acid is to be added, wherein it dissolves readily by aid of gentle heat. This solution is to be poured into a small volume of cold water and the platinum it contains precipitated by hydrogen sulphide at or near boiling temperature. After filtering and cooling, ammonia is added till the titanium is just precipitated, and a measured volume, containing a known weight of absolute sulphuric acid, is then added—just enough to redissolve the precipitate. The solution is then made up with acetic acid in such amount that the final bulk shall contain from 7 to 11 per cent of absolute acid, and then enough solid sodium acetate is stirred in to more than take up the sulphuric acid introduced. On rapidly bringing the liquid to ebullition the titanium is precipitated in flocculent and easily filterable condition, and the precipitation is complete after a minute's boiling, provided all the prescribed conditions have been followed and zirconium is absent.

The precipitate is washed first with acetic acid of 7 per cent strength and then with hot water. After fifteen to twenty minutes' ignition over a good burner it is in condition for weighing and will lose no more weight over the blast lamp. For large amounts of titanium a repetition of the sodium-carbonate fusion, etc., should be made. The actual carrying out of all these operations, when once the method is understood, requires much less time than the detailed description would indicate.

β. Gooch's method not directly applicable to rocks containing zirconium.—Prior to the adoption of the colorimetric method, Gooch's was invariably used in the Survey laboratory. Occasional inability to secure clean and complete precipitation by it was experienced,

¹ This operation will probably free the precipitate from any vanadium that may be present, which F. J. Pope (Trans. Am. Inst. Min. Eng., vol. 29, 1899, p. 372) says is carried down with the titanium to some extent.

especially with a certain series of rocks rather poor in titanium. Long search showed the difficulty to be due to the presence of zirconium, which acts as a marked preventive of the precipitation of titanium by boiling in an acetic-acid solution under the conditions of the Gooch method.

The above rocks were found to contain up to 0.2 per cent of ZrO_2 , and this amount was able to prevent precipitation of 0.3 per cent of TiO_2 . The titanium which came down in excess of this amount did not settle out in flocculent condition, as happens when zirconium is not present, and it was difficult to filter. After the removal of the zirconium, however, in the manner to be hereafter described (16. A, p. 173), no difficulty was experienced in precipitating all the titanium with the usual ease.

b. THORNTON'S METHOD.

α. Preliminary remarks.—W. M. Thornton,¹ in order to obviate the need of destroying the tartaric acid that the Gooch method calls for and the attendant introduction of a large amount of manganese, extended earlier work by himself and I. Bellucci and L. Grassi² so as to effect a very satisfactory separation of titanium from aluminum and phosphorus, after prior separation of iron according to 9. E (p. 124), and defined the requisite acidity and volume of the solution. His test results are excellent, and it seems as if the method might well supersede that of Gooch. Thornton's method has an advantage over Gooch's in that the operations are reduced in number and that zirconium is also precipitated quantitatively.³ Applying the method to zirconium, Thornton and E. M. Hayden⁴ found that some phosphorus, if present, is precipitated with the zirconium. This observation has been confirmed by G. E. F. Lundell and H. B. Knowles at the Bureau of Standards, but they found that although in a 5 per cent sulphuric acid solution the error is appreciable, in one of 10 per cent strength it is of the order of only half a milligram when operating with a decigram or more of ZrO_2 and 2 centigrams of P_2O_5 . Hence, considering the very small amount of zirconium that is usually encountered in rocks, it seems unnecessary to modify the method so as to exclude error from this source alone.

However, Lundell and Knowles found that vanadium is precipitated to a considerable extent in both the quadrivalent and quinivalent states, more in the latter than in the former, that dissolved silica is appreciably precipitated with titanium and zirconium, and

¹ Am. Jour. Sci., 4th ser., vol. 37, 1914, p. 407; Chem. News, vol. 110, 1914, p. 5; Zeitschr. anorg. Chemie, vol. 87, 1914, p. 375.

² Gazz. chim. ital., vol. 43, pt. 1, 1913, p. 570.

³ Schroeder, K., Zeitschr. anorg. Chemie, vol. 72, 1911, p. 95.

⁴ Am. Jour. Sci., 4th ser., vol. 38, 1914, p. 137; Chem. News, vol. 110, 1914, p. 153; Zeitschr. anorg. Chemie, vol. 89, 1914, p. 377.

that neither boron nor hexavalent uranium is precipitated. The procedure of Thornton therefore needs slight modification, as introduced below, in order to care at one stroke for possible errors arising from the presence of the interfering elements. According to Lundell and Knowles, thorium and cerium are precipitated partially, but in rock analysis these may be disregarded.

β. *Procedure*.—To the filtrate from the iron sulphide (9. E, p. 124) is added about 40 cm.³ of sulphuric acid (1:1), and the hydrogen sulphide thus liberated is boiled out. After cooling to 10° to 15° the solution is made up with water to 400 cm.³ and a cold 6 per cent solution of "cupferron" (ammonium nitrosophenylhydroxylamine) is added slowly, with constant stirring. The beaker is set aside for the precipitate to settle, and the supernatant liquid is then tested by adding a few drops of the reagent. The formation of a white precipitate indicates that the reagent is in excess, whereas a yellow turbidity shows the precipitation to be incomplete. It is well also to test the filtrate. The precipitate is collected on a filter paper, using gentle suction, and washed 20 times with cold hydrochloric acid (made by diluting 100 cm.³ of acid of specific gravity 1.20 to 1 liter). After having been sucked dry at the pump, the precipitate and filter are dried completely in a platinum crucible at 110°. With the crucible not quite covered by the lid, the ignition is begun with a very small flame. After the first violent gush of smoke the heat is raised a little, when the destructive distillation will proceed quietly. When the carbon is burned off the residue is fused with sodium carbonate, the melt extracted with water, the solution filtered, and the insoluble matter washed with water containing a little sodium carbonate. The contents of the filter are dissolved in sulphuric acid and the precipitation by "cupferron" is repeated. From the finally purified and weighed oxides the zirconium can be separated and determined according to 16. A (p. 173), and the titanium measured by colorimetry, as in 14. B. d (p. 159), or either one can be determined and the other found by difference. In the latter case it is better to determine the zirconium rather than the titanium, as the former is usually present in very small amount and any slight error incurred in determining the titanium would throw a large relative error upon the zirconium.

Thornton and Hayden fuse phosphatic materials containing zirconium with sodium carbonate, leach with water, and apply the "cupferron" separation to the sulphuric acid solution of the residue.

Thornton's results seem to indicate that alkali salts are carried down with titanium (and presumably with zirconium) to a slight extent, and Lundell and Knowles have confirmed this indication. The error so caused will be very small, indeed, and usually negligible in rock analysis. When the contamination is likely to be of moment

the precipitate should be fused with sodium carbonate, the melt extracted with water, the residue washed and dissolved in acid, and the precipitation repeated, or preferably, perhaps, the titanium and zirconium should be precipitated first by ammonia, filtered, dissolved in sulphuric acid, and then precipitated by "cupferron."

James Brown¹ has described modifications of the "cupferron" method for separating zirconium, titanium, iron, manganese, and aluminum, which he applied to the analysis of zircon and baddeleyite.

C. BASKERVILLE'S METHOD.

The excellent method of Charles Baskerville for separating titanium and zirconium from iron and aluminum has been referred to in section 10, under E. a (p. 130). Baskerville says in the first of his papers:

If a neutralized solution of titanium and iron chlorides of not too great dilution be boiled with an excess of sulphur dioxide, the iron becomes deoxidized at once and a white flocculent precipitate of titanium separates out.

The method can be applied to a hydrochloric acid solution of one or more of the oxides obtained according to section 8 (p. 106). It has not been determined whether sulphur dioxide is necessary when iron is absent, but probably it is not, although it may assist to keep aluminum in solution. Phosphorus will accompany the titanium and zirconium if present, but can be removed by fusing the ignited precipitate with sodium carbonate and extracting with water. Either titanium or zirconium, or both, can then be determined in the insoluble salts, after filtering, by methods described above and also under "Zirconium" (p. 172) and "Phosphorus" (p. 177).

D. METHOD OF DITTRICH AND FREUND.

A method proposed by M. Dittrich and S. Freund has been described under 10 E. b (p. 131). In view of the required absence of aluminum, its use is restricted.

D. VOLUMETRIC METHODS.

a. GENERAL CONSIDERATIONS.

Many writers have proposed or worked upon the development of volumetric methods for titanium, all based upon reduction of the titanium to the trivalent state. The probable reason why these methods did not receive at once extended recognition lies in the difficulty and uncertainty that attached to the procedure employed for effecting reduction and preventing premature reoxidation of the reduced titanium. The difficulty was overcome as to sulphate solu-

¹ Jour. Am. Chem. Soc., vol. 39, 1917, p. 2358.

tions by passing the hot solution through a Jones reductor into a flask connected with a suction pump and kept filled with carbon dioxide, or into a solution of ferric sulphate in such a manner as to prevent all contact with air—that is, by having the tip of the reductor long enough to reach beneath the surface of a solution of ferric sulphate in the receiving flask with which the reductor is connected. Which of these procedures to adopt depends upon the particular volumetric method that is to be used. Presumably the use of the reductor is permissible with methods that call for a hydrochloric acid solution of titanium.

P. W. and E. B. Shimer¹ were the first to use the reductor in determining titanium. They avoided contact of the titanous solution with air by keeping the flask full of carbon dioxide, and recommended an exceptionally long (36-inch) and very narrow ($\frac{3}{8}$ -inch bore) reductor tube, filled with amalgamated zinc granules of sizes that pass a sieve of 10 meshes to the linear inch and remain on one of 20 meshes. Other workers have found that the ordinary and shorter form of reductor gives entire satisfaction, even without using carbon dioxide, when a titration method is to be used which permits collecting the titanous solution in one of ferric sulphate. It is only necessary that the tip of the reductor be made long enough to discharge the titanous solution beneath the surface of the ferric sulphate solution in the receiving flask.

The titanous and ferric salts react at once, with formation of ferrous sulphate equivalent to the titanium.

The volumetric methods have the great advantage that in general they are applicable in the presence of iron and aluminum. They can be used to best advantage in rock analysis on the ignited and weighed precipitate of the oxides of iron, aluminum, etc., or on the titanium that has been separated from the mixture in a more or less pure state by a gravimetric method. The only interfering elements likely to be present are vanadium and chromium, which can be removed by making a fusion with sodium carbonate and extracting the alkali chromate and vanadate with water.

In the following sections reference is made, as a rule, only to the later papers on the several subjects. Suffice it to mention, among earlier authors, F. Pisani,² F. W. Hinrichsen,³ and H. D. Newton.⁴ Hinrichsen reduced in hydrochloric acid with a magnesium-zinc alloy (50-50) and titrated with ferric chloride solution.

For rock and mineral analysis it is probable that methods c and d, described below, will be found more convenient than method b.

¹ Eighth Internat. Cong. Appl. Chemistry, 1912, vol. 1, p. 445.

² Compt. Rend., vol. 59, 1864, p. 298.

³ Chem. Zeitung, vol. 31, 1907, p. 738.

⁴ Am. Jour. Sci. 4th ser., vol. 25, 1903, p. 130.

D. METHYLENE BLUE METHOD.

Eva Hibbert¹ applied to the determination of titanium a volumetric method which had been worked out earlier by E. Knecht² for another purpose. B. Neumann and R. K. Murphy,³ seemingly unaware of Hibbert's work, developed an essentially identical method. Oxidation of titanous chloride in an atmosphere of carbon dioxide by means of a standardized solution of methylene blue is the basis of the method. Knecht and Hibbert use a solution containing about 2 grams of methylene blue to the liter; Neumann and Murphy use one containing 3.9 or 7.8 grams, corresponding to 1 and 2 mg. of Ti respectively. The appearance of a blue color indicates complete oxidation of the titanium even in the presence of ferrous iron, which is not oxidized by methylene blue. The titanous solution is formed from the titanite by reduction with zinc and hydrochloric acid. The authors carry out the reduction in a flask, but a better way would seem to be to pass the titanite solution through a zinc reductor (see a, above) into a receiver filled with carbon dioxide.

The titration can be conducted hot in a strong hydrochloric acid solution. The end point is not sharp in nitric or sulphuric solutions. The method is applicable in the presence of silica, iron, and other basic metals, also of antimony, arsenic, and phosphorus, but molybdenum, vanadium, tungsten, chromium, and tin interfere.

The standardization of the methylene blue solution is made against a "commercial" titanous chloride solution, of which the titanium content must be determined by a gravimetric method or by titration with a standard solution of ferric alum. (See c, below.)

C. FERRIC ALUM METHOD.

A method quite equal to the foregoing, according to Knecht,⁴ and likewise applicable in the presence of silica, iron, and aluminum, is that of G. Gallo,⁵ based on the oxidation of titanous chloride by ferric alum in the presence of potassium thiocyanate as indicator. Knecht's titrating solution contains 14 grams of ferric alum and 5 cm.³ of concentrated sulphuric acid in a liter and is standardized by permanganate, after reduction, or by titanous chloride.

The titanium-bearing material (according to Knecht), after being brought into hydrochloric acid solution, is first reduced by zinc and then titrated cold with the ferric alum solution.

¹ Jour. Soc. Chem. Industry, vol. 28, 1909, p. 189. See also Knecht, E., and Hibbert, E., New reduction methods in volumetric analysis, London, Longmans, Green & Co., 1910.

² Jour. Dyers and Col., vol. 21, 1905, p. 5.

³ Zeitschr. angew. Chemie, vol. 26, pt. 1, 1913, p. 613.

⁴ Idem, p. 734.

⁵ Atti Accad. Lincei, vol. 16, pt. 1, 1907, p. 325.

The Shimers (see a, above) say that when the reduction is effected in the long zinc reductor "the time required for complete reduction need not be more than 15 minutes." They proceed as follows:

The reductor is first washed out with hot dilute sulphuric acid, whereby the zinc is heated and the reduction is made more effective. The receiving flask is then filled with carbon dioxide, whereupon the reductor is connected and the hot sulphuric solution of iron and titanium is drawn through it, but not faster than by rapid dropping. Several portions of hot water containing a little sulphuric acid are passed through the reductor and then carbon dioxide is again introduced rapidly. Finally, when cool, at least 5 cm.³ of a saturated solution of potassium thiocyanate is added and the titration with ferric alum is carried out. The end reaction is rather slow, and the solution must be added until a brownish color remains for at least a minute. With large quantities of iron the solution must be put twice through the reductor.

d. PERMANGANATE METHOD.

The Shimers also titrate both iron and titanium with permanganate after reducing as described in the last paragraph, and in the same solution determine either the iron alone by permanganate after reducing the iron with hydrogen sulphide, boiling out the excess of the latter and cooling in an atmosphere of carbon dioxide (see 9. c, p. 119) or the titanium as in c, above.

This method has been used satisfactorily by the Shimers in cooperative analyses of the steels and irons that are issued by the Bureau of Standards as standards for analysis.

If titanium is the only reducible substance present, the operation is simpler, and it is preferable to let the reduced solution enter the receiving flask under the surface of a ferric sulphate solution. (See a, above.) In this case it is advantageous to add syrupy phosphoric acid to the ferric solution in order to obtain a sharper end point in the permanganate titration. This mixture may be prepared in advance by dissolving the sulphate and phosphoric acid in water in the proportion of 100 grams of the sulphate and 150 cm.³ of the acid in a liter. The procedure as communicated by James A. Holladay, of the Electro-Metallurgical Co., is essentially as follows:

A reductor of the ordinary type having been washed out with dilute (2.5 per cent) sulphuric acid and water, the receiver is charged with 10 cm.³ of the prepared ferric solution, the reductor is inserted into the flask so that its tip enters the liquid, and connection is made with the suction pump. The stopcock of the reductor is then opened and there are poured, in order, into the funnel of the reductor the following solutions: 100 cm.³ of warm sulphuric acid (2.5 per cent),

the warm titanium solution (about 50 cm.³ in volume and containing 10 per cent of sulphuric acid), 200 cm.³ of the dilute sulphuric acid, and 50 cm.³ of water. The funnel of the reductor should be allowed at no time to become empty and the stopcock should be closed while some of the water still remains above the zinc.

A blank is run in the same way, except that 50 cm.³ of 10 per cent sulphuric acid is substituted for the titanium solution. The permanganate should be standardized against sodium oxalate, such as is furnished by the Bureau of Standards.

15. BARIUM (ZIRCONIUM, RARE EARTHS, TOTAL SULPHUR, CHROMIUM).

The five constituents barium, zirconium, rare earths, total sulphur, and chromium can be determined with great economy of time and labor in the same portion of rock powder, of which a 2-gram portion should be used, though if vanadium is to be looked for it will be best to determine it and chromium in a different portion (20. C, p. 185). It has been said (12. C, p. 145) that only in very exceptional cases will barium be found with the calcium and strontium after two or possibly three precipitations of the latter as oxalate, since it passes into the filtrates with the magnesium, whence it may be obtained as sulphate after removal of ammoniacal salts. Addition of some alcohol insures also the simultaneous recovery of traces of strontium if the rocks are very rich in it; but it is unsafe to regard the amount of barium thus separated from the magnesium as representing the total amount in the rock. It will almost always be found lower than the truth, probably for the reason that there are opportunities during the analysis for slight losses.

A. THE GENERAL METHOD.

Decomposition is effected by fusing the 2-gram portion with sulphur-free sodium carbonate and an amount of niter insufficient to injure the crucible (0.5 to 1 gram), first over the Bunsen flame, then over the inclined blast, the crucible being fitted snugly into a hole in a disk of platinum foil or asbestos board (fig. 3, p. 34) to prevent access of sulphur from the gas flame. In case sulphur is not to be regarded, the niter and disk are omitted. After thorough disintegration of the melt in water, to which a drop or two of methyl or ethyl alcohol has been added for the purpose of reducing manganate, the solution is filtrated and the residue washed with a very dilute solution of sodium carbonate free from bicarbonate. This is to prevent turbid washings. A yellow color in the filtrate indicates chromium.

After reduction of the manganate by alcohol the filtrate contains silica, alumina, and all the other acid constituents except titanium,

also a very little iron, but the separation of these from the remaining constituents is not always quantitative, never so as to silica and alumina. The proportions of these two which go into the aqueous extract vary greatly according to their relative proportions in the original material and the amounts and character of the bases other than alumina. For instance, with alkali feldspars much of each dissolves, but with pure kaolinite very little of either. With most rocks both filtrate and residue contain large amounts of both.

(For the further treatment of the filtrate see "Sulphur," 26. C, p. 231, and "Chromium," 19. B, p. 182.)

The residue is washed from the paper into a small beaker without removing the filter from the funnel and is digested with little more than enough warm dilute sulphuric acid to effect solution of all soluble constituents (stronger acid may be used and in larger amount if barium only is sought). If zirconium is to be determined, the amount of acid used at this stage and later should be measured, so as to permit control of the concentration given under 16. A. b (p. 173). A few drops of sulphurous acid are added at the same time to effect solution of the brown hydroxide of manganese. There will remain undissolved more or less residue. Care must be taken not to digest so long with acid as to cause gelatinization of the dissolved silica. The liquid is passed through the original filter and collected in an Erlenmeyer flask of 100 to 150 cm.³. The paper with its contents after washing is ignited, evaporated with hydrofluoric and sulphuric acids together, and the final residue taken up with a little hot dilute sulphuric acid. All the barium will remain undissolved, besides some of the strontium and perhaps a good deal of calcium. This is collected on a small filter and the filtrate added to the former one, which now contains all the zirconium and rare earths. (For its further treatment see 16. A, p. 173, and 17. A, p. 176.)

The residue last obtained is ignited and fused with sodium carbonate, leached with water, and the residue dissolved off the filter by a few drops of hydrochloric acid, from which solution the barium is thrown out by a large excess of sulphuric acid. A single solution of the ignited barium sulphate in concentrated sulphuric acid and reprecipitation by water suffices to remove traces of calcium which might contaminate it if the rock was one rich in calcium, and even strontium is seldom retained by it in quantity sufficient to give concern. Should this be the case, however, which will occur when the SrO and BaO are together in the rock in, roughly speaking, 0.2 and 0.4 per cent, respectively, the only satisfactory way is to convert the sulphates into chlorides and to apply to the mixture the ammonium-chromate method of separation (12. D, p. 145).

Barium and strontium sulphates can be brought into a condition for testing spectroscopically by reducing for a very few moments the whole or part of the precipitate on a platinum wire in the luminous tip of a Bunsen burner, then moistening with hydrochloric acid and testing in the usual manner. This test should not be omitted.

The procedure outlined in the foregoing paragraphs for the determination of barium in silicate rocks and its separation from calcium and strontium is the one which long experience has shown to be best adapted for securing the most satisfactory results with a minimum expenditure of time.¹ Even where no attempt is made to separate contaminating traces of strontium and barium one from the other, the error is usually of no great consequence, for an absolute error of even 25 per cent in a substance constituting only 0.1 or 0.2 per cent of a rock is ordinarily of small moment compared with the ability to certify to its presence with approximate correctness.

With such small amounts of barium as are usually found in rocks it is doubtful if Mar's method² for the separation of barium from calcium and magnesium by the solvent action of concentrated hydrochloric acid mixed with 10 per cent of ether on the chlorides could be conveniently applied here, although for larger amounts the method would seem to be accurate and easily executed. Moreover, it would probably not entirely remove contaminating strontium, and hence offers no advantage.

B. THE METHOD WITHOUT REGARD TO ZIRCONIUM AND SULPHUR.

If zirconium and sulphur are not to be looked for, the simplest procedure is to decompose the powder by sulphuric and hydrofluoric acids (see 14. B. c. 2, p. 158, under "Titanium") and to complete the purification of the barium sulphate thus obtained in the manner described in the fourth paragraph of A, above.

16. ZIRCONIUM.

Zirconium is seldom looked for by chemists, though shown by the microscope to be one of the most constant rock constituents, usually in the form of zircon, in which occurrence its amount can be approximately judged and a chemical test rendered almost unnecessary; but sometimes it occurs in other minerals, and is then unrecognizable under the microscope. In most exceptional cases it may be present up to a few per cent of the rock, rarely reaches 0.2 per cent, and is usually much less than 0.1 per cent.

¹ For details consult Hillebrand, W. F., Jour. Am. Chem. Soc., vol. 16, 1894, p. 83; Chem. News, vol. 69, 1894, p. 147.

² Am. Jour. Sci., 3d ser., vol. 43, 1892, p. 521.

A. AUTHOR'S METHOD.

a. PRELIMINARY REMARKS.

For its detection and estimation in such cases, or whenever a search for it seems called for, the following procedure, resulting from an attempt to use a method of G. H. Bailey,¹ has been devised, which serves, when carried out with care, to detect with certainty the merest trace—0.02 per cent, for instance—in 1 gram. The precipitant is a soluble orthophosphate.

The preliminary treatment of the rock powder has been fully given under "Barium" (15. A, p. 170), where the separation from barium has been described and also the concentration of the zirconia in a small amount of dilute sulphuric solution.

In earlier editions of this work the statement was made that the precipitation should be made in a solution containing only a small amount of sulphuric acid, probably not much more than 1 per cent. George Steiger² has shown, however, that precipitation is complete in presence of as much as 3 per cent of the acid, and more recently P. Nicolardot and A. Reglade³ have found that it is complete with even 20 per cent of acid (by weight). This higher acidity has the advantage of preventing contamination of the precipitate by titanium, iron, and chromium. According to Nicolardot and Reglade separation from aluminum is complete with 10 per cent of acid.

G. E. F. Lundell, in studying the method at the Bureau of Standards, found that the composition of the precipitate is affected by the amount of precipitant used and by the manner of washing. With not less than 10 times the theoretical amount of precipitant the composition is uniformly such, after washing with ammonium nitrate solution, that on ignition it yields $Zr_2P_2O_7$, containing 46.3 per cent of ZrO_2 . With less precipitant the composition is variable, although precipitation is complete if twice the theoretical amount is used. Lundell found also that washing with pure water extracts phosphorus. Nicolardot and Reglade used in their tests 1 gram of ammonium phosphate, which they prefer to sodium phosphate, although the latter precipitates zirconium completely.

b. PROCEDURE.

To the solution, which should be in a small flask or beaker and contain about 20 per cent by weight of sulphuric acid, is added hydrogen peroxide to oxidize the titanium and then at least ten times the theoretical amount of a soluble alkali orthophosphate in

¹ Jour. Chem. Soc., vol. 49, 1886, pp. 149, 481.

² Jour. Washington Acad. Sci., vol. 8, 1918, p. 637.

³ Compt. Rend., vol. 168, 1919, p. 348.

water solution. The ammonium salt is preferred. Ordinarily 1 gram of the precipitant may be used. The solution is then kept tepid for 2 hours. If the solution bleaches after a time more hydrogen peroxide should be added. Under these circumstances the zirconium is thrown out as phosphate and collects as a flocculent precipitate. If it can be assumed to be free from titanium and iron the precipitate may be filtered, washed thoroughly with water containing ammonium nitrate (5 per cent), ignited, and weighed as $Zr_2P_2O_7$ (46.3 per cent ZrO_2). For the amounts of zirconium met with in rocks the phosphate may be ignited without special precautions, but if the amount is large, such as is obtained with ores of zirconium, marked decrepitation occurs, which makes it necessary to ignite up to a certain point in a tightly covered crucible. Even then slight loss may be suffered. (For the treatment of the filtrate see "Rare-earth metals," 17. A, p. 176.)

If there is reason to think that the precipitate is not pure it is collected on a filter, ignited, fused with sodium carbonate, and leached with water. The insoluble matter collected on a filter is washed, ignited, and fused with potassium or sodium pyrosulphate. The melt is dissolved in sulphuric acid of 20 per cent strength, a little hydrogen peroxide is added, and the precipitation with alkali phosphate is repeated. Naturally the volume of the solution should be gaged by the amount of the zirconium. For most rocks it need not exceed 20 cm.³ Titanium is now almost never present, and the zirconium soon appears as a colorless flocculent precipitate in a fit condition to be collected and weighed as phosphate.

If there is doubt of the precipitate having the normal composition, especially if large, or if the qualitative identification of zirconium is desired, the following procedure is in order. Fuse with sodium carbonate, leach, ignite, fuse with pyrosulphate, reprecipitate by ammonia, and weigh as ZrO_2 . Certainty as to its identity can be had by again bringing it into solution, precipitating by ammonia, dissolving in hydrochloric acid, evaporating to a drop or two, and testing with turmeric paper or by a microchemical reaction. With the very smallest amounts no color can be obtained by this turmeric-paper test, which, however, responds readily to as little as 1 mg. of dioxide and with proper care for as small an amount as 0.3 mg. (H. N. Stokes). No element other than thorium is ever likely to contaminate the zirconium thus precipitated.

The above-described method is applicable to the separation of zirconium, if present, in the mixture of it and titanium obtained by the methods of Thornton (14. C. b, p. 164), of Baskerville (14. C. c, p. 166, and B, below), and of Dittrich and Freund (14. C. d, p. 166).

In Bailey's experiments the precipitation was not made by addition of a phosphate but is said to be due solely to the hydrogen peroxide, the precipitate being a hydrated peroxide, Zr_2O_5 , or ZrO_3 .¹ My own efforts as well as those of others to secure a precipitate in acid solutions of zirconium sulphate by hydrogen peroxide alone have been unsuccessful, except in very concentrated solutions and with 30 per cent peroxide. The ability to obtain the zirconium free from phosphoric acid would certainly be a great improvement on the method described above.

B. OTHER METHODS.

G. Streit and B. Franz² claimed to secure complete separation of titanium from iron and zirconium by boiling the neutralized solutions of the sulphates with a large excess (50 per cent) of acetic acid. The method has been recommended from time to time, but without any data showing its value. The single separation made by Streit and Franz was far from perfect.

J. T. Davis³ separated zirconium sharply from aluminum, though not from iron, by precipitation as an oxyiodate in a boiling neutralized solution of chlorides, but the method has not been studied further.

C. Baskerville⁴ proposed a method for the separation of zirconium from iron and aluminum similar to his method for the separation of titanium from those elements (14. C. c, p. 166). It is based on the precipitability of zirconium by boiling the neutralized chloride solution for two minutes in presence of sulphurous acid, and seems to be excellent. As titanium is always present and is quantitatively thrown down also, the two would have to be separated by hydrogen peroxide and a soluble phosphate. No tests as to the availability of the method for separating the small amounts met with in rock analysis have been made, but M. Dittrich and S. Freund have used it successfully in slight modification for larger amounts (14. C. d, p. 166), and have also devised a method for the direct separation of zirconium from titanium by precipitation with ammonium salicylate.⁵

The "cupferron" method of Thornton, as given under "Titanium" (14. C. b, p. 164), can be used also for the precipitation of zirconium alone or in company with titanium, but how accurate it is for the final determination of the very small amounts that occur in rocks is still to be ascertained.

J. D. Ferguson⁶ determines zirconium in ores and alloys by precipitation with either phenylhydrazine (see 10. D. a, p. 128) in hydro-

¹ Chem. News, vol. 60, 1889, p. 6.

² Jour. prakt. Chemie, vol. 108, 1869, p. 65.

³ Am. Chem. Jour., vol. 11, 1889, p. 27.

⁴ Jour. Am. Chem. Soc., vol. 16, 1894, p. 475; Chem. News, vol. 70, 1894, p. 57.

⁵ Zeitschr. anorg. Chemie, vol. 56, 1907, p. 344.

⁶ Eng. and Min. Jour., vol. 106, 1918, p. 793.

chloric acid solution or with sodium phosphate in sulphuric acid solution (see A, above) and defines carefully the procedure in each method. He finds that results by the two methods agree well. He seems to have worked under conditions giving a precipitate of uniform composition by the phosphate method but takes no account of titanium in the phenylhydrazine method. If the ores he worked with held no titanium the last factor does not enter.

17. RARE-EARTH METALS OTHER THAN ZIRCONIUM.

If it is necessary to look for rare earths other than zirconia, the following procedures will prove satisfactory and not at all difficult.¹

A. USUAL METHOD.

The filtrate from the zirconium phosphate (16. A, p. 173) or, if zirconium is not to be determined, the earlier solution (15. A, p. 170) is treated with excess of potassium hydroxide to precipitate the rare earths and ferric and titanous oxides, while retaining the silica and alumina in solution. After settling, the liquid is decanted and the precipitate is washed once or twice by decantation and slightly on the filter. The precipitate is washed from the paper into a small platinum dish, treated with hydrofluoric acid, and the liquid evaporated nearly to dryness. A little water with a few drops of hydrofluoric acid is added and the insoluble rare-earth fluorides (crude) are collected on a small filter held by a perforated platinum or rubber cone and washed with water acidified with the same acid. The precipitate is washed into a small platinum dish and evaporated to dryness with sulphuric acid, the paper being burned and added before expulsion of the acid. The sulphates are dissolved in dilute hydrochloric acid, the rare-earth hydroxides precipitated by ammonia, redissolved in hydrochloric acid, the solution evaporated to dryness, and the residue heated with a few drops of a solution of oxalic acid. Anything that may be present except the rare earths dissolves readily, these remaining as insoluble oxalates. If there is a doubt as to the complete separation of the alkaline earths the ignited oxalates may be dissolved in hydrochloric or nitric acid, precipitated by ammonia, redissolved in whichever one of the acids may have been used, the solution evaporated to dryness, the oxalates reprecipitated, ignited, and the resulting oxides weighed.

¹ M. Dittrich (Ber. Deutsch. chem. Gesell., vol. 41, 1908, p. 4373) calls attention to the fact that ferric, aluminum, and chromic, as well as uranic compounds prevent precipitation of cerium and presumably other rare-earth metals as oxalate, unless a very large excess of the precipitant is used, but that with such excess precipitation is complete. Salts of these metals even dissolve cerium oxalate, but excess of oxalic acid or ammonium oxalate throws it out again. This behavior need hardly be considered in the procedures here given.

The amounts are too small to permit separation into further groups, but the presence of cerium can be readily shown if a strong yellow color develops on heating the ignited oxides with strong sulphuric acid.

B. ALTERNATIVE METHOD.

The rock powder is thoroughly decomposed by several partial evaporations with hydrofluoric acid, the transparent precipitate of silico-fluorides and of the fluorides of all earth metals except zirconium is collected on a platinum cone, washed with water acidulated by hydrofluoric acid, washed back into the dish or crucible, and evaporated with enough sulphuric acid to expel all fluorine. The filter is burned and the ash added. By careful heating the excess of sulphuric acid is removed and the sulphates are taken up by dilute hydrochloric acid. The rare earths, with perhaps some alumina, are then precipitated by ammonia, washed, redissolved in hydrochloric acid, and evaporated to dryness, then taken up with water and a drop of hydrochloric acid, and only enough ammonium acetate to neutralize the latter added, followed by oxalic acid (not ammonium oxalate, which would fail to precipitate thorium). In this way as little as 0.03 per cent of rare earths has been found when working on not more than 2 grams of material.

18. PHOSPHORUS.

A. PRELIMINARY REMARKS.

It is sometimes possible to extract all phosphorus from a rock by simple digestion with nitric acid, but not always; hence the necessity for resorting to one of the longer methods of extraction detailed below. Whatever method is used great care is required in order to obtain accurate results.

Unless the utmost economy of material is called for it is unadvisable to determine the phosphorus in the mixture of oxides obtained as described in section 8, but an independent portion of the rock sample should be used. Furthermore, phosphorus should never be determined in any solution that has been obtained from a fusion with alkali bisulphate or pyrosulphate, or after fuming with sulphuric acid, because these operations cause a loss of P_2O_5 (see second paragraph under 9. A, p. 115), either by volatilization (as metaphosphoric acid) or by reversion to metaphosphoric acid without volatilizing. In the latter event the subsequent treatment of the solution may not effect its complete retransformation to the orthophosphate state, in which alone is the ordinary precipitation by magnesia mixture applicable.

B. PROCEDURE WHEN MATERIAL IS AMPLE.**B. WASHINGTON'S METHOD OF PRELIMINARY TREATMENT.**

About 1 gram of rock powder is decomposed in a platinum dish or capacious crucible with dilute nitric and hydrofluoric acids. When all gritty particles have disappeared the solution is evaporated to dryness and reevaporated with nitric acid two or three times to decompose fluorides and silicofluorides to a considerable extent.¹ The residue is treated on the bath with dilute nitric acid and eventually filtered from any undissolved matter. This last should be for precaution's sake always ignited, fused with a little sodium carbonate, extracted with water, and the extract acidified with nitric acid and added to the main solution. (For further treatment see c, below.)

B. ALTERNATIVE METHOD OF PRELIMINARY TREATMENT.

Fuse with sodium carbonate, separate silica by a single evaporation with nitric acid, treat the ignited silica with hydrofluoric and nitric acids, evaporate to expel hydrofluoric acid, repeat the evaporation with nitric acid alone two or three times, bring the small residue into solution by boiling with nitric acid and add it to the main portion.

C. SUBSEQUENT TREATMENT.

Add to the solution obtained in a or b ammonium nitrate and molybdate solution as ordinarily prescribed, and allow to stand at a temperature of not over 40° for 12 hours, or until it is certain that precipitation is complete.

The precipitate is filtered on paper and washed with water containing 5 per cent ammonium nitrate and 1 per cent nitric acid, after which it is transferred by a jet of water to a small beaker, which is then placed under the funnel containing the filter paper. The paper is washed with dilute ammonia water and two or three times with pure water. If the ammonia is insufficient to dissolve the whole of the yellow precipitate in the beaker, more ammonia is added, and if a clear solution does not result the liquid is passed through the same filter in order to collect the insoluble matter.

The turbidity often observed on dissolving the precipitated and washed phosphomolybdate in ammonia is due to a compound of phosphorus. If the addition of a small fragment of a crystal of citric or tartaric acid fails to dissolve it, this should always be fused with sodium carbonate, extracted with water, and the filtrate otherwise treated as above, in order to obtain the phosphorus in it.

¹ The method as originally described in Washington's "Manual of the chemical analysis of rocks" has been modified by Washington and by me independently to the extent of doing away with the filtration of the precipitate of silicofluorides and fluorides before proceeding with the evaporation.

Hydrochloric acid is added to the ammoniacal filtrate until the yellow precipitate begins to reappear and does not redissolve quickly, and then a slight excess of magnesia mixture. Ammonia is now added slowly with continuous stirring until the precipitation of magnesium-ammonium phosphate has been largely accomplished. About one-fifth the volume of strong ammonia solution is then added, and after a little further stirring the beaker is set aside for some hours. The precipitate is then collected on a paper filter and washed with ammonia solution of about 2.5 to 3 per cent strength (roughly, 1 volume strong ammonia water to 9 volumes water).

If a reprecipitation is necessary, which will seldom be the case in rock analysis, the first precipitate of magnesium-ammonium phosphate is not collected on a filter, but the supernatant liquid is decanted through the filter which is later to be used, the precipitate in the beaker is dissolved in a little hydrochloric acid, a drop or two of magnesia mixture is added, then ammonia, and the final precipitation is made as at first. (For ignition, etc., of the precipitate, see this subject under "Magnesium," 13. B, p. 150.)

Vanadium, if present, is not only precipitated with phosphorus by the molybdate reagent, but it renders the precipitation of the phosphorus incomplete. Further, the mixed precipitate is affected differently by wash solutions than the pure phosphomolybdate. J. R. Cain and J. C. Hostetter¹ devised a method for the determination of vanadium in steels which is based on the complete precipitation of vanadium with a large excess of phosphorus. An orange color of the phosphomolybdate betrays the presence of vanadium. However, in rocks the vanadium content is so low that ordinarily its effect may be disregarded. If the unexpected case should present itself works on steel analysis should be consulted, in particular a paper by J. R. Cain and F. H. Tucker,² who effect perfect separation of the phosphorus after reducing the vanadium in a particular manner.

C. PROCEDURE WHEN MATERIAL IS SCANTY.

The following procedure admits of determining in the same portion not only phosphorus but also barium, iron, vanadium, chromium, and titanium, the last two either colorimetrically or gravimetrically, and is in large part extracted from a paper by T. M. Chatard.³

¹ Tech. Paper Bur. Standards No. 8, 1913; Jour. Ind. Eng. Chemistry, vol. 4, 1912, p. 250.

² Tech. Paper Bur. Standards No. 24, 1913; Jour. Ind. Eng. Chemistry, vol. 5, 1913, p. 647.

³ Am. Chem. Jour., vol. 13, 1891, p. 106; Bull. U. S. Geol. Survey No. 78, 1891, p. 87; Chem. News, vol. 63, 1891, p. 267.

Silica is removed by hydrofluoric and sulphuric acids, excess of fluorine expelled¹ (6 A. a, footnote, p. 90), the residue brought into solution as far as possible with sulphuric or hydrochloric acid and hot water, filtered, the residue ignited, fused with sodium carbonate, dissolved in hydrochloric acid, and the solution, after precipitation of barium, added to the main one, which is now precipitated by ammonia to get rid of the magnesium salts usually present, and thus insure a cleaner subsequent fusion with sodium carbonate.

The precipitated Al_2O_3 , P_2O_5 , Cr_2O_3 , Fe_2O_3 , ZrO_2 , and TiO_2 are dissolved in hot hydrochloric acid and filtered into a large platinum crucible, the filter is burned and added, the solution evaporated to pastiness, a little water added to dissolve the salts, and dry sodium carbonate added in portions and stirred in thoroughly to prevent lumpiness in the fusion to follow, which is continued for half an hour. Addition of sodium nitrate is not necessary.

The fused mass is boiled out with water and filtered and the insoluble matter is washed with very dilute sodium-carbonate solution. In the residue iron and titanium can be determined by the methods already described.² In the filtrate chromium can be determined colorimetrically if present in sufficient amount to give a pronounced color. (See 19. B, p. 182.) Afterward, or immediately if the chromium is not to be thus estimated, enough ammonium nitrate is added to react with all the carbonate, and the solution is digested on the bath till most of the ammonium carbonate is gone. Nearly if not quite all alumina is thus thrown out, carrying with it all the phosphorus. The precipitate is washed with dilute ammonium-nitrate solution till the yellow color wholly disappears, after which it is dissolved in nitric acid and the phosphorus thrown out by molybdate solution. The filtrate from the aluminum and phosphorus, containing chromium and most of the vanadium, can be treated as detailed in the following sections.

Tests made by G. E. F. Lundell at the Bureau of Standards have shown that some of the vanadium is precipitated with the aluminum. Perhaps a second precipitation would reduce the amount to a negligible quantity.

19. CHROMIUM.

If vanadium is absent, or nearly so, as it is likely to be in those highly magnesian rocks (peridotites) which usually carry a good deal of chromium, the following separation and gravimetric method for chromium gives good and concordant results, but in the presence

¹ The expulsion of fluorine should be made without excessive volatilization of sulphuric acid, so as to avoid loss of P_2O_5 . (See 9. A, p. 116.)

² See 9. C. b, pp. 122-123, concerning recovery of a small amount of iron that may have passed into the alkaline filtrate.

of vanadium, and it is best generally to assume its presence, the colorimetric method should always be adopted.

A. GRAVIMETRIC METHODS.

a. AUTHOR'S METHOD.

Having obtained chromium in solution as chromate and free from all else but a little alumina, as at the conclusion of the preceding section on phosphorus, proceed as follows:

Concentrate if necessary and add fresh ammonium sulphide, or introduce hydrogen sulphide. The chromium is reduced and appears as a precipitate of sesquioxide mixed with the rest of the alumina. This precipitate is now treated, according to H. Baubigny,¹ by dissolving in nitric acid, evaporating nearly to dryness and heating with strong nitric acid and potassium chlorate, finally evaporating to dryness to get rid of the acid. Oxidation is complete and very speedy. On dilution with cold water, sodium bicarbonate is added in slight excess, and after two or three hours the precipitated alumina is filtered off. From the filtrate the chromium is then thrown out by fresh ammonium sulphide, redissolved, reprecipitated to free from alkali, and weighed.

b. JAKOB'S METHOD.

W. Jakob² recommends the following method for the precipitation of aluminum (and evidently of ferric iron, titanium, zirconium, and manganese) and its separation from chromium. To the hydrochloric-acid solution containing the equivalent of 0.1 to 0.2 gram of Al_2O_3 and 20 to 100 cm.³ in volume, in an Erlenmeyer flask of 100 to 300 cm.³ capacity, is added drop by drop a freshly prepared solution of sodium hydroxide (about 5 per cent strength) till the aluminum hydroxide formed redissolves. Avoid an excess. The solution is then boiled, and saturated bromine water is added, drop by drop at first in order not to lower the temperature of the solution too much and so produce a slimy precipitate. Toward the end the bromine may be added faster until the solution remains red. The excess bromine is then boiled out, the liquid is filtered, and the precipitate is washed with hot water. Precipitate adhering to the glass is loosened by a little nitric acid and reprecipitated by ammonia. Some chromium is carried down with the aluminum but can be removed, after decanting, by boiling for a few minutes with water containing ammonium nitrate and ammonia. It is possible that a

¹ Bull. Soc. chim., new ser., vol. 42, 1884, p. 291; Chem. News, vol. 50, 1885, p. 18.

² Zeitschr. anal. Chemie, vol. 52, 1913, p. 651.

little aluminum may be redissolved by this treatment. The combined precipitates are ignited and weighed.

The chromium can be determined in the filtrate by applying the treatment given under *a*, above.

Magnesium and zinc, if present, are partly precipitated with the aluminum. Jakob claims that small amounts of these can be removed by the treatment with ammonium nitrate and ammonia. In the presence of sulphates and borates the method is unsatisfactory.

B. COLORIMETRIC METHOD.

For the colorimetric method, which is very accurate and by far the quickest method¹ for determining chromium in rocks and ores where the amount does not exceed a few per cent, there is needed the aqueous extract of a sodium-carbonate fusion of the rock (as obtained, for instance, in the manner explained under "Phosphorus," C, p. 179, or under A, above) in order to compare its color with that of a standard solution.

a. Preparation and strength of standard solution.—This standard solution is made by dissolving 0.25525 gram or double that amount of pure potassium monochromate in 1 liter of water made alkaline by a little sodium carbonate. Each cubic centimeter then corresponds to 0.1 or 0.2 mg. of chromic oxide (Cr_2O_3), in which condition chromium is usually reported in rocks and ores. It is probably inadmissible to increase the strength of the standard much above the higher of the figures given.

β. Preparation of the test solution.—Before filtering the aqueous extract of the sodium-carbonate fusion a few drops of alcohol (ethyl or methyl) are added to destroy the color of sodium manganate. If the yellow color of the filtrate is very faint, concentration by evaporation will strengthen it, and less than 2 mg. of chromic oxide in 1 gram of rock can then be determined exactly. For smaller amounts it is best to employ from 3 to 5 grams of powder and then to concentrate the chromium by precipitation by mercurous nitrate, as detailed in the next section under "Vanadium" (20. C, p. 185); otherwise it may be difficult or impossible, because of the large amount of alkali carbonate present, to obtain a filtrate of sufficiently small bulk to show a decided color.

If niter has been used in the fusion and the crucible has been at all attacked by it, a yellow coloration of the filtrate may be due to dissolved platinum, but neither the proportion of niter nor the tempera-

¹ Hillebrand, W. F., Jour. Am. Chem. Soc., vol. 20, 1898, p. 454; Chem. News, vol. 78, 1898, pp. 227, 239; Bull. U. S. Geol. Survey No. 167, 1900, p. 37. First applied by L. de Koningh (Nederl. Tyds. voor Pharm., Chem. en Tox., 1889) for the estimation of chromium in foodstuffs.

ture of the blast should ever be high enough to permit the crucible to be attacked. A passing yellowish coloration of the filtrate, due to this or some other cause,¹ is not to be ascribed to chromium.

If it is desired to use the solution obtained as in either A. a or A. b, above, there will be no need to add alcohol, for manganese is absent.

γ. *Comparison of colors.*—The final solution is transferred to a graduated flask, which is then filled to the mark with water. The flask should be of such size that the color of the oxidized solution shall be weaker than that of the standard chromium solution. Definite amounts of the latter are then diluted with water from a burette until of the same strength as the test solution, exactly as described on page 37. For very minute amounts it may be necessary to use Nessler tubes, as in ammonia estimations, instead of the glasses and apparatus there described and depicted.

As with colorimetric methods in general, this one gives better results with small than with large percentages of chromium, yet it can be applied in the latter cases with satisfactory results by making a larger number of consecutive comparisons with the same solution.²

C. COMPARATIVE DATA.

A few comparisons between colorimetric and gravimetric determinations of chromium are here given to show the order of agreement, the former having been made several months and even years after the latter.

Percentage determinations of chromium (Cr_2O_3).

Gravimetric.	Colorimetric.
Trace.	0.018
0.05	.051
.14	.12
.08	.083
Trace.	.013
None.	.0036
None.	.0067

The outcome was somewhat surprising, for it was hardly to be expected that the long and laborious quantitative separations should have resulted so well. It should be mentioned that for the gravimetric tests but 1 or 2 grams at most were used, which accounts for the reported absence of chromium in two instances, this report being based on the lack of color in the aqueous extract of the alkali fusion after removal of manganese.

¹ Consult McBride, R. S., and Scherrer, J. A., Jour. Am. Chem. Soc., vol. 39, 1917, p. 928.

² D. W. Horn has studied the "Variable sensitiveness in the colorimetry of chromium." See Am. Chem. Jour., vol. 35, 1906, p. 253; vol. 36, 1906, p. 196.

20. VANADIUM (CHROMIUM) AND MOLYBDENUM.

A. DISTRIBUTION OF VANADIUM AND MOLYBDENUM.

The wide distribution of vanadium throughout the earth's crust has been clearly established in recent years (see pp. 22-23), not only in ores and in coals, but in clays, limestones, sandstones, and igneous rocks.¹ I have shown that vanadium occurs in appreciable amounts in the more basic igneous and metamorphic rocks up to 0.08 per cent or more of V_2O_5 , but that it seems to be absent or nearly so from the highly siliceous rocks. Some of their ferric aluminous silicate constituents carry still higher percentages—up to 0.13 per cent V_2O_5 in a biotite separated from a pyroxenic gneiss. Molybdenum, on the other hand, appears to be confined in quantities susceptible of detection to the more siliceous rocks, and except perhaps in rare instances is not present in them in quantitatively determinable amount when operating on 5 grams of material. Hence the quantitative search for vanadium will usually be limited to rocks with less than 60 per cent of silica. The search for it even then will perhaps not often warrant the necessary expenditure of time, but in this connection it is to be remembered that neglect to determine it introduces an error in the figures for both ferrous and ferric oxides, which in extreme cases may be of considerable moment. (See 9. C. b, p. 121; 21. D. c. β, p. 202.)

B. CONDITION OF VANADIUM IN ROCKS.

The connection below and elsewhere mentioned of vanadium with the ferric aluminous silicates of rocks, taken in connection with the existence of the mineral roscoelite, classed as a vanadium mica, indicates that the vanadium corresponds in condition to aluminum and ferric iron, and that it is to be regarded as replacing one or both of these elements. Hence it should be reported as V_2O_5 and not as V_2O_3 .

What its condition may be in matter of secondary origin, like clays, limestones, sandstones, coals, and ores of iron, is yet open to discussion. It was my opinion at one time that it should be regarded as in the pentavalent state (V_2O_5), but my work on certain remarkable vanadiferous sandstones² of western Colorado, in which it unquestionably occurs as trivalent vanadium (V_2O_3), has led to a decided unsettling of this view. It is proper to recall that C. Czudnowicz,³ because of the extreme difficulty in completely extracting it from iron ores by an alkali-carbonate fusion and because of the easy reducibility of vanadic acid by ferrous salts, under the conditions in which brown iron ores are supposed to form, considered the vanadium in

¹ Hillebrand, W. F. Distribution and quantitative occurrence of vanadium and molybdenum in rocks of the United States: *Am. Jour. Sci.*, 4th ser., vol. 6, 1898, p. 209; *Chem. News*, vol. 78, 1898, p. 216; *Bull. U. S. Geol. Survey* No. 167, 1900, p. 49.

² Hillebrand, W. F., and Ransome, F. L., *Am. Jour. Sci.*, 4th ser., vol. 10, 1900, p. 120; *Bull. U. S. Geol. Survey* No. 262, 1905, p. 9.

³ Poggendorff's *Annalen*, vol. 120, 1863, p. 20.

such ores to be in a lower condition of oxidation (V_2O_3). O. Lindemann's contrary conclusion¹ with regard to certain iron ores, because the vanadium was extracted as V_2O_5 by sodium-carbonate fusion without niter, is not valid, since this would probably be the case even if it existed in the ore as V_2O_3 .

C. AUTHOR'S METHOD.

a. DESCRIPTION OF THE METHOD.

In the following method there is nothing absolutely novel except that chromium and vanadium, when together, need not be separated, but are determined, the former colorimetrically, as already described (19. B, p. 182), the latter volumetrically, in the same solution.²

Five grams weight of the rock is thoroughly fused over the blast with 20 of sodium carbonate and 3 of sodium nitrate. After extracting with water and reducing manganese with alcohol it is probably quite unnecessary, if the fusion has been thorough, to remelt the residue as above, though for some magnetites and other ores containing larger amounts of vanadium than the generality of rocks this may be necessary, as Edo Claassen has shown.³ The aqueous extract is next nearly neutralized by nitric acid, the amount to be used having been ascertained conveniently by a blank test with exactly 20 grams of sodium carbonate, etc., and the solution is evaporated to approximate dryness. Care should be taken to avoid overrunning neutrality, because of the reducing action of the nitrous acid set free from the nitrite produced during fusion, but when chromium is present it has been my experience that some of this will invariably be retained by the precipitated silica and alumina, though only in one case have I observed a retention of vanadium, it being then large. The use of ammonium nitrate, instead of nitric acid, for converting the sodium carbonate into nitrate does not seem to lessen the amount of chromium retained by the silica and alumina.

As a precautionary measure, therefore, and always when chromium is to be determined also, the silica and alumina precipitate should be evaporated with hydrofluoric and sulphuric acids, the residue fused with a little sodium carbonate, and the aqueous extract again nearly neutralized with nitric acid and boiled for a few moments, the filtrate being added to the main one.

Mercurous nitrate is now added to the cold alkaline solution in some quantity, so as to obtain a precipitate of considerable bulk, containing, besides mercurous carbonate, chromium, vanadium, molybdenum, tungsten, phosphorus, and arsenic, should all happen to be in the rock. The mercurous carbonate serves to counteract any acidity

¹ Dissertation, Jena, 1878, through *Zeitschr. anal. Chemie*, vol. 18, 1879, p. 99.

² Hillebrand, W. F., *Jour. Am. Chem. Soc.*, vol. 20, 1898, p. 461; *Chem. News*, vol. 78, 1898, p. 295; *Bull. U. S. Geol. Survey No. 167*, 1900, p. 44.

³ *Am. Chem. Jour.*, vol. 8, 1886, p. 437.

resulting from the decomposition of the mercurous nitrate. Precipitating in a slightly alkaline instead of a neutral solution renders the addition of precipitated mercuric oxide unnecessary for correcting this acidity. If the alkalinity, as shown by the formation of an unduly large precipitate, should have been too great, it may be reduced by careful addition of nitric acid until an added drop of mercurous nitrate no longer produces a cloud.

After heating and filtering, the precipitate is ignited in a platinum crucible after drying and removing from the paper to obviate any chance of loss of molybdenum and of injury to the crucible by reduction of arsenic. The residue is fused with a very little sodium carbonate, leached with water, and the solution, if colored yellow, filtered into a graduated flask of 25 cm.³ or more capacity. The chromium is then determined accurately in a few minutes by comparing with a standard alkaline solution of potassium monochromate (19. B, p. 182). Then, or earlier in absence of chromium, sulphuric acid is added in slight excess, and molybdenum and arsenic, together with occasional traces of platinum, are precipitated by hydrogen sulphide, preferably in a small pressure bottle.¹ If the color of the precipitate indicates absence of arsenic the filter with its contents is ignited carefully in porcelain, and the delicate sulphuric-acid test for molybdenum is applied as follows: The molybdenum compound is heated in porcelain with a single drop of strong sulphuric acid till the acid is nearly volatilized. On cooling the appearance of a beautiful blue color is proof of the presence of molybdenum.

The filtrate, in bulk from 25 to 100 cm.³, is boiled to expel hydrogen sulphide, and titrated at a temperature of 70° to 80° with a very dilute solution of permanganate, representing about 1 mg. of V₂O₅ per cubic centimeter, as calculated from the iron strength of the permanganate, one molecule of V₂O₅ being indicated for each one of Fe₂O₃. One or two checks are always to be made by reducing again by means of a current of sulphur-dioxide gas, boiling this out again,² and repeating the titration. The latter results are apt to be a very little lower than the first and are to be taken as the correct ones.

The cause of the difference was attributed to extraction of oxidizable matter from the paper, and this view has been confirmed by R. S.

¹ From a sulphuric solution the separation of platinum and molybdenum by hydrogen sulphide is much more rapid and satisfactory than from a hydrochloric solution.

² The direct use of a solution of sulphur dioxide or of an alkali sulphite is inadmissible unless these have been freshly prepared, for after a lapse of time they contain other oxidizable bodies than sulphurous acid or a sulphite. The sulphur dioxide is best obtained as wanted by heating a flask containing a solution of sulphur dioxide, or of a sulphite to which sulphuric acid has been added.

³ The expulsion of the last trace of sulphur dioxide is said to be accomplished more effectively by boiling with simultaneous passage of a rapid current of carbon dioxide for a few minutes at the last than by boiling alone. Because of the small amount of air carried with it, long passage of the gas is said to result in slight oxidation of the vanadium (Manasse, O., *Ann. Chem. u. Pharm.*, vol. 240, 1887, p. 23; *Zeitschr. anal. Chemie*, vol. 32, 1893, p. 225.)

McBride and J. A. Scherrer¹ in work undertaken at my suggestion at the Bureau of Standards. These authors found that the effect could be eliminated almost wholly by first passing as little as 25 cm.³ of water through the paper and completely with a larger amount. The use of a platinum-felted perforated (Munroe) crucible should also eliminate the error.

b. CONFIRMATORY QUALITATIVE TESTS.

In case the volume of permanganate used is so small as to make doubtful the presence of vanadium, it is necessary to apply a qualitative test, which is best made as follows: The solution is evaporated and heated to expel excess of sulphuric acid, the residue is taken up with 2 or 3 cm.³ of water and a few drops of dilute nitric acid, and a couple of drops of hydrogen peroxide are added. A characteristic brownish tint indicates vanadium. Unless the greater part of the free sulphuric acid has been removed the appearance of this color is sometimes not immediate and pronounced, hence the above precaution. It is also necessary that the nitric acid shall be in considerable excess, since in a neutral or only faintly acid solution the color does not appear strongly.

The above is a surer test to apply than the following: Reduce the bulk to about 10 cm.³, add ammonia in excess, and introduce hydrogen sulphide to saturation. The beautiful cherry-red color of vanadium in ammonium-sulphide solution is much more intense than that caused by hydrogen peroxide in acid solution, but the action of ammonia is to precipitate part or all of the vanadium with the chromium or aluminum that may be present or with the manganese used in titrating, and ammonium sulphide is unable to extract the vanadium wholly from these combinations. Usually, however, the solution will show some coloration, and addition of an acid precipitates brown vanadium sulphide, which can be collected, ignited, and further tested if desired.

c. APPLICATION OF THE METHOD IN PRESENCE OF RELATIVELY MUCH CHROMIUM.

The application of the method in its foregoing simplest form is subject to one limitation—the chromium must not be present above a certain moderate amount. This limitation is due to the considerable amount of permanganate then required to produce a clear transition tint when titrating in a hot solution, as is advisable with vanadium. In a cold solution of chromic sulphate much less permanganate is needed to produce the peculiar blackish tint without a shade of green, which affords a sure indication of excess of permanganate, but in a hot and especially a boiling solution the oxidation of the chromium itself takes place so rapidly that a very large excess of the reagent

¹ Jour. Am. Chem. Soc., vol. 39, 1917, p. 928.

may be added before a pronounced end reaction is obtained. Nevertheless, fairly satisfactory determinations of as little as 1 or 2 mg. of vanadium pentoxide can be made in presence of as much as 30 mg. of chromic oxide. To accomplish this it is only necessary to apply a simple correction obtained by adding permanganate to a like bulk of equally hot chromic sulphate solution containing approximately the same amount of chromium.

C. H. Ridsdale¹ titrated the cold solution to avoid oxidation of chromium and obtained accurate results, but in my experience the end reaction is then uncertain.

The following tables contain the results of a considerable number of tests, those in Table 2 being tabulated separately in order to show the degree of accuracy attainable with a large excess of chromium by applying the correction mentioned above and also the amount of this correction:

TABLE 1.—Tests for vanadium in the presence of chromium.

No.	Chromic oxide.	Vanadium pentoxide.	Vanadium pentoxide found.	Error.	No.	Chromic oxide.	Vanadium pentoxide.	Vanadium pentoxide found.	Error.
	<i>Milligrams.</i>	<i>Milligrams.</i>	<i>Milligrams.</i>	<i>Milligram.</i>		<i>Milligrams.</i>	<i>Milligrams.</i>	<i>Milligrams.</i>	<i>Milligram.</i>
1	1	9.37	9.22	-0.15	7	3.5	18.74	18.97	+0.23
2	1	.94	1.04	+ .10	8	6	5.6	6.1	+ .50
			.98	+ .04	9	6	4.68	4.78	+ .10
3	1.5	5.25	5.49	+ .24	10	6	5.62	5.58	- .04
			5.43	+ .19	11	10	5.62	5.58	- .04
4	2	5.62	5.5	- .12	12	10	23.52	23.81	+ .29
			5.5	- .12				23.71	+ .19
5	3	4.68	4.78	+ .10	13	10	46.85	46.98	+ .13
			4.78	+ .10				47.20	+ .35
			4.83	+ .15	14	25	23.52	23.65	+ .13
6	3	5.62	5.58	- .04				23.75	+ .23
			5.58	- .04	15	87.5	23.52	23.71	+ .19
7	3.5	18.74	18.89	+ .15					

TABLE 2.—Application of correction for larger amounts of chromium, obtained by adding potassium permanganate to an equal bulk of solution containing a like amount of chromic sulphate.

No.	Chromic oxide.	Vanadium pentoxide.	Vanadium pentoxide found.		Error.	Volume of solution.
			Uncorrected.	Corrected.		
	<i>Milligrams.</i>	<i>Milligrams.</i>	<i>Milligrams.</i>	<i>Milligrams.</i>	<i>Milligram.</i>	
16	20	0.94	1.59	0.99	+0.05	50 to 100 cm. ³
17	20	1.87	2.69	2.09	+ .22	50 to 100 cm. ³
			2.39	1.79	- .08	
			2.59	1.99	+ .12	
18	20	18.74	19.4	18.73	- .01	50 to 100 cm. ³
			19.3	18.63	- .11	
			19.3	18.63	- .11	
19	30	1.87	2.99	2.14	+ .27	About 100 cm. ³
			2.79	1.94	+ .07	
			2.79	1.94	+ .07	
			2.69	1.84	- .03	
			2.69	1.84	- .03	
20	30	1.87	2.69	1.79	- .08	200 cm. ³
			2.89	2.09	+ .22	
			2.89	2.09	+ .22	
21	62	46.85	2.79	1.99	+ .12	200 cm. ³
			48.90	47.60	+ .75	

¹ Jour. Soc. Chem. Industry, vol. 7, 1888, p. 73.

In spite of the fact that the correction in most of the trials of this last table represents a large proportion of the permanganate used, the results must be considered satisfactory in view of the small amount of vanadium present, and they show that the method in competent hands after a little experience affords trustworthy figures.

The method of T. Fischer¹—digestion of the precipitated lead salts with a strong solution of potassium carbonate—appears to offer the long-needed satisfactory quantitative separation of arsenic, phosphorus, chromium, tungsten, and molybdenum from vanadium, the normal lead metavanadate remaining quite unattacked, according to Fischer, while the other lead salts are wholly decomposed, but the applicability of this method to the separation of the minute amounts often found in rocks and ores has not been tested. The object has been in the present case to reach satisfactory results with the greatest expedition, and when chromium is not present in considerable amount this is accomplished.

Fortunately chromium is almost never a prominent constituent of clays, coals, iron ores, and those rocks in which vanadium has thus far been reported, for although it is usually certain of the most basic of the silicate rocks that are highest in chromium—as the peridotites—yet in these, so far as present experience teaches, vanadium is lacking, a fact doubtless connected with the simultaneous absence from them of ferric aluminous silicates.

D. COLORIMETRIC METHOD FOR VANADIUM.

In the paper already cited² the possibility of a colorimetric method for vanadium, based on its behavior toward hydrogen peroxide, was suggested. L. Maillard³ has since developed such a method, though it has not been tested in the Survey laboratory.

21. FERROUS IRON.

A. OXIDATION OF FERROUS IRON IN MINERALS BY GRINDING—PREPARATION OF SAMPLE.

As already pointed out under 3. C (p. 60), the effect of grinding in air is to lower the FeO and increase the Fe_2O_3 in a mineral powder that contains FeO .⁴ Of the latter 20 to 30 per cent or more may thus be caused to disappear by grinding steadily for two hours. Attempts to prevent this chemical change by grinding under water, alcohol, and carbon tetrachloride have been partly successful, but not enough so to permit the substitution in general practice of one

¹ Inaugural dissertation, Rostock, 1894.

² Hillebrand, W. F., Jour. Am. Chem. Soc., vol. 20, 1898, p. 461; Chem. News, vol. 78, 1898, p. 295; Bull. U. S. Geol. Survey No. 167, 1900, p. 44.

³ Bull. Soc. chim., vol. 23, 1900, p. 559.

⁴ Cf. Mauzelius, R., Sveriges Geol. Undersökning, Arsbok I, No. 3, 1907; Hillebrand, W. F., Jour. Am. Chem. Soc., vol. 30, 1908, p. 1120; and Chem. News, vol. 98, 1908, pp. 205, 215.

of these media for air. Grinding in a wholly inert atmosphere, such as nitrogen (not carbon dioxide, which I find seems to form carbonates), might be successful in preventing oxidation in large part, if not wholly, but is quite impracticable for general work. That it would not prevent taking up both loosely and firmly held water on subsequent contact of the powder with the air is certain, as such absorption is due to increased surface exposure. From the fact that oxidation is greatly lessened by grinding under one of the above-named liquids, even though the powder be then exposed to air, it follows that increased surface exposure is not the dominant factor in promoting oxidation, but probably local heating as the grains are fractured and rubbed under the pestle. The effect seems to be influenced also by the hardness of the iron minerals and those associated with them, and perhaps still more by the chemical nature of the iron-bearing molecules themselves.

The following table contains some selected and typical data, taken from the paper already cited,¹ that show the effect on the FeO content of grinding different rocks under different conditions and also the comparative merits of the Pratt and Cooke methods of determining ferrous iron:

Effect of grinding on the ferrous-iron content of rock powders.

Material and maximum size of grain of bulk sample.	Conditions of grinding.				FeO (per cent).	
	No.	Grams.	Time (minutes)	Medium.	Pratt method.	Cooke method.
Basalt, 0.08 mm.	1a	Unground.			7.03, 7.07, 7.09, 7.11	
	1b	4	30	Abs. alc.	7.09, 7.12, 7.14	
	1c	4	30	Air.	7.01, 7.07, 7.08, 7.16, 7.18, 7.23	
	1d	4	120	Air.	6.84, 6.90	
Diorite, 0.08 mm.	2a	Unground.			3.65, 3.65	3.55, 3.52
	2b	4	120	Abs. alc.	3.47, 3.49	3.40, 3.49
	2c	4	120	CCl ₄ .	3.30, 3.37	3.25, 3.30
	2d	4	140	H ₂ O.	3.40, 3.43	3.36, 3.38
	2e	4	120	Air.	3.28, 3.36, 3.40	3.29, 3.38
Diabasic norite or gabbro..	3a	Unground.			13.55, 13.35	13.54
	3b	4	20	Abs. alc.	13.00, 13.10, 13.11,	13.11
	3c	4	60	CCl ₄ .	13.16, 13.19	
	3d	4	30	Air.	12.91, 12.93, 13.06, 13.07	13.06, 13.07
	3e	4	120	Air.	12.59, 12.66	
Andesite, 0.08 mm.	4a	Unground.			3.32, 3.34	
	4b	4	50	Air.	3.09	
Altered basaltic green-stone, 0.18 mm.	5a	Unground.			6.68	
	5b	4	120	Air.	3.64	
Quartz diorite, 0.11 mm.	6a	Unground.			2.58	
	6b	4	120	Air.	1.67	
	7a	Unground.			2.08, 2.09	
	7b	4	120	Abs. alc.	2.01, 2.01	
	7c	4	30	Air.	2.04, 2.07	
	7d	4	120	Air.	1.47, 1.47	
Altered basaltic rock, 0.18 mm.	8a	Unground.			8.33, 8.34	
	8b	4	120	Abs. alc.	8.11, 8.14	
	8c	4	30	Air.	8.23	
	8d	(?)	(?)	Air.	5.74	

¹ Jour. Am. Chem. Soc., vol. 30, 1908, p. 1120; Chem. News, vol. 98, 1908, pp. 205, 215.

The experiments carried out by me show several things: (1) Although comparatively brief grinding (15 to 30 minutes) in air and long grinding under alcohol do not, as a rule, yield powders that are markedly oxidized (sometimes almost no oxidation seems to have taken place), this is not always so; hence grinding under one or the other of these media can not be recommended as a practice to follow at all times. The data for short and long grinding in the same enveloping medium are not strictly comparable, as the former was done by hand, the latter by a more effective mechanical process. (2) Alcohol, in spite of its greater solvent power for oxygen, seems to be a little more effective in preventing oxidation than water. It has the further advantage that it can be removed more quickly afterward. (3) Of the organic media employed alcohol seems to be more efficacious than carbon tetrachloride. (4) The effect of the presence of refractory iron-bearing minerals (garnet and others) is indicated by the rather wide variations in duplicate determinations, as shown under 1 and 3 of the table, when the material is not in a fine state of division. (5) The agreement that can be expected in duplicate determinations by either the Pratt or the Cooke method is excellent with fine powders or with coarse powders that yield readily to attack by hydrofluoric acid. (6) Inasmuch as powders so fine as to pass sieves of 30 and even 60 meshes to the linear centimeter often show much less than 0.1 per cent of moisture if hydrous alteration products are absent it is reasonable to conclude that in their preparation there has been occasioned relatively as little oxidation of ferrous iron as absorption of moisture, on the assumption that the small amount of water found results from the increased surface exposure due to crushing and is not inherent. Therefore if the powder is completely decomposed by hydrofluoric acid it is safe to assume that a determination of ferrous iron in it carried out with proper precautions will give a result close to the truth when other disturbing factors are not in evidence. (7) With different minerals very different degrees of oxidation are brought about under like conditions—from a few per cent (1d) up to about 45 per cent (5b) of the FeO after several hours' grinding—and it is not always the mineral that might a priori be regarded as most oxidizable that shows most oxidation. (See paper cited.) Further, a soft or tough mineral undergoes greater oxidation if ground with a hard one than by itself alone.

It is plain that nearly all mineral analyses which have been made in the past are affected by more or less serious errors in respect not only to the oxides of iron but also to water, the error being greater the further the comminution of the sample was carried. Very many analyses show ferric iron in minerals that should apparently contain

none and small amounts of water for which there seems to be no place in any probable formula. These are discordances for which a simple and in most cases probable explanation is now offered. A revision of much past analytical work, particularly that relating to iron minerals, is called for, but before it can be properly done adequate provision must be made to avoid the old errors. In the paragraphs following are set forth the procedures that seem best adapted to attain this end in the light of present experience. Much routine and experimental work, must, however, yet be done before rules to fit all cases can be formulated. It is perhaps advisable to add here, in order to prevent misconception, that the errors in past work are not as a rule to be assumed equal to those in the above table that resulted from grinding for two hours or more, for few, if any, analysts have made it a rule to grind for such a length of time.

The mineral powder that has been prepared by crushing without grinding (3. B, p. 57) serves as the starting point. If trial shows that gentle boiling of it for 20 minutes with hydrofluoric acid leaves no residue or but little, this sample is to be used directly for the ferrous iron determination. If the residue is considerable, a weighed portion (0.5 to 1.0 gram) of the sample is to be ground with absolute alcohol in a large agate mortar only long enough to yield a powder that will leave little or no residue. The alcohol is then to be allowed to evaporate spontaneously, and when the last trace has disappeared the powder is to be transferred to a platinum crucible of 80 to 100 cm.³ capacity, the powder which may adhere to the mortar and pestle being also transferred by the aid of a fine jet of hot water. The subsequent operations are given under the respective methods (D, below), which are those involving decomposition by hydrofluoric acid. The Mitscherlich method (C, below) requires in almost every case a very fine powder. For this and other reasons that method finds little application. For the same reason the modifications of the hydrofluoric acid method that require a powder of considerable fineness (D. d. β , γ , δ) will be less applied than the one (D. d. α) which permits the use of a relatively coarse powder. If a very fine powder must be employed, there seems to be no way known at present of correcting for whatever oxidation may have taken place during grinding. It will be preferable in such cases to grind under alcohol a small weighed portion of the coarse sample, instead of grinding a large portion and taking from this an aliquot part, the reason being that in the latter case separate determinations of both loosely and firmly held water must be made in order to be able to correct the FeO found for the considerable weight of water taken up during grinding (4. B, p. 69).

B. COMPARISON OF SEALED-TUBE AND HYDROFLUORIC-ACID METHODS—
COMPARATIVE WORTHLESSNESS OF THE FORMER IN ROCK ANALYSIS.

No point in rock analysis has been the cause of greater solicitude to the chemist, and especially to the mineralogist and petrographer, than the determination of iron in ferrous condition. The sealed-tube or Mitscherlich method with sulphuric acid, for a long time the only available one, is in theory perfect, since complete exclusion of oxygen is easily attainable. Its earliest recognized defect lies in the inability to secure always complete decomposition of the iron-bearing minerals, and even to ascertain, oftentimes, whether or not the decomposition has been complete. The addition of hydrofluoric acid to the sulphuric in the tube, in order to insure this breaking up, is to be regarded as of very doubtful utility in most cases, since the glass may be so strongly attacked as to add an appreciable amount of iron to the solution, and the hydrofluoric acid may have exhausted itself in attacking the glass before the more refractory minerals succumb. Nevertheless, if decomposition can be effected by sulphuric acid alone the results obtained are sharp and concordant; but they are in rock analysis usually higher than when made by any of the modifications of the hydrofluoric-acid method now so extensively practiced. This difference is not very marked with rocks containing but 1 or 2 per cent of ferrous iron, but it increases with rising percentage to such an extent that where the sealed-tube method will show 12 per cent ferrous oxide the other may indicate no more than 10 per cent. This is a fact of which I have long been cognizant, but it seems not to have been known to chemists or petrographers at large, though E. A. Wülfing¹ noticed this difference in certain analyses without appreciating its significance. Experiments with soluble iron salts of known composition, like ferrous sulphate and ferrous-ammonium sulphate, throw no light on the subject, for both methods give with them the same sharp and accurate results.

The key to the problem was discovered by L. L. de Koninck² a good many years ago but remained unknown to the chemical world by reason of its obscure medium of publication until rediscovered by H. N. Stokes in the Survey laboratory during an investigation on the action of ferric salts on pyrite and other sulphides.³ That oxidation of the sulphide and reduction of the ferric salt hereby takes place was also recognized by J. H. L. Vogt,⁴ but not the ease with which the change takes place and the completeness of the oxidation of the pyrite, not only of its iron but of the greater part of the sulphur as well. Pure pyrite itself is attacked with extreme

¹ Ber. Deutsch. chem. Gesell., vol. 32, 1899, p. 2217, footnote.

² Ann. Soc. géol. Belgique, vol. 10, 1882-83, p. 101; Zeitschr. anorg. Chemie, vol. 26, 1901, p. 123.

³ Bull. U. S. Geol. Survey No. 186, 1901; Am. Jour. Sci., 4th ser., vol. 12, 1901, p. 414.

⁴ Zeitschr. prakt. Geologie, 1899, pp. 250-251.

slowness by boiling dilute sulphuric and hydrofluoric acids, either alone or mixed, but the moment a ferric salt is introduced the case is altogether different.

The complete solution to the problem was afforded by the observation made in the Survey laboratory that rocks with hardly an exception and many minerals carry pyrite or pyrrhotite, or both, often in considerable amount, often in traces only. Sulphur can almost always be detected in 2 grams of rock powder.

Experiment has shown (D. c. z, p. 201) that with the amounts of sulphides usually found in igneous rocks their effect on the estimation of ferrous iron by the hydrofluoric-acid method at atmospheric pressure and boiling heat is negligible, though by increasing the amount of sulphide the effect becomes more and more apparent, because of the greater surface of pyrite exposed to the action of the ferric iron of the rock.

Under the conditions of the Mitscherlich method, on the other hand—a temperature of 150 to 200°, and even higher, high pressure, much longer time of action, and impossibility of escape of any hydrogen sulphide that may be formed—the sulphur of the sulphides becomes nearly if not fully oxidized to sulphuric acid at the expense of the ferric iron in the rock, with the production of an equivalent amount of ferrous iron in addition to that resulting from the sulphide itself.

Let us now see what the effect of these traces of sulphides when fully oxidized amounts to. One atom of sulphur (32) requires for its complete conversion to trioxide the oxygen of three molecules of ferric oxide (480), which then becomes 6 molecules of ferrous oxide (432). In other words, 0.01 per cent of sulphur may cause the ferrous oxide to appear too high by 0.135 per cent, and 0.10 per cent of sulphur may bring about an error of 1.35 per cent in ferrous oxide. The case is still worse if the sulphur is set free as hydrogen sulphide from a soluble sulphide, for then the above percentages of sulphur produce errors of 0.18 and 1.8 per cent, respectively, in the ferrous oxide determination.

The error caused by sulphides tends to become greater the more there is present of either or both sulphide and ferric salt. Now, the highly ferruginous rocks usually carry more ferric iron than the less ferruginous ones, and they are often relatively high in pyrite and pyrrhotite; hence the increasing discrepancy between the results by the two methods as the iron contents of the rocks rise is fully in accord with the above explanation.¹

¹ For details of experiments showing the worthlessness of the Mitscherlich method for rocks and minerals which contain even a trace of free sulphur or sulphides, see Hillebrand, W. F., and Stokes, H. N., Relative value of the Mitscherlich and hydrofluoric acid methods for ferrous-iron determinations: *Jour. Am. Chem. Soc.*, vol. 22, 1900, p. 625; and *Zeitschr. anorg. Chemie*, vol. 25, 1900, p. 326.

Of course carbonaceous matter will, under the conditions of the Mitscherlich method, likewise reduce sulphuric acid and cause the determination of ferrous iron to be faulty.

Notwithstanding the fact that the Mitscherlich method has thus been discredited in its general applicability to rocks and minerals, it is still probably the best with those which are totally free from sulphides and wholly decomposable. Hence the conditions under which success can best be achieved by it are set forth in the following paragraphs.

C. THE MODIFIED MITSCHERLICH METHOD.

α. Strength of acid.—The method in its original and usual application calls for a mixture of 3 parts of sulphuric acid and 1 of water by weight, or about 3 to 2 by volume, though a still stronger acid is sometimes used. In some cases, however, perhaps in most, much better decomposition of the silicates is effected by reversing the proportions of water and acid, or at any rate by diluting considerably beyond the above proportion. Hereby the separation of salts difficultly soluble in the stronger acid is avoided and the actual solvent effect on the minerals seems to be in no wise diminished.

β. Filling, sealing, and heating of the tube.—The very finely powdered mineral having been introduced into a tube of resistant glass free from ferrous iron, the open end is drawn out, so as to leave a funnel for the introduction of the acid. A very little water is then introduced and carefully heated to boiling for a moment to expel all air from the powder. The diluted acid—which has just been boiled down from a state of greater dilution in order to have it free from air—is then poured in until the tube is about three-fourths filled. Carbon dioxide free from hydrogen sulphide is then introduced, from a generator which has been in active operation for some time, through a narrow glass tube drawn out of the same kind of glass as that of which the decomposing tube consists. In a few moments the air is expelled, and the small tube is then sealed into the large one over the blast lamp without interrupting the gas current until the very last instant, when to prolong it would perhaps cause a blowing out of the softened glass. The interruption of the current at the proper moment is easily effected by the pressure of the thumb and finger holding the small tube at the point where it enters the rubber tube leading from the gas generator. No breakage in the oven ever occurs as a consequence of thus fusing one tube into the other.

The heating is done in a bomb oven at any desired temperature up to, say, 200°, and continued at intervals until examination by aid

of a low-power lens shows that decomposition is complete or has progressed as far as can be hoped for. By inclosing the glass in an outer tube of strong steel, properly capped¹ and containing a little ether or benzine to equalize the pressure on both sides of the glass, the temperature can be elevated far beyond what is otherwise permissible, and the decomposition will then doubtless be more complete with refractory silicates.

γ. *Reason for introducing gas and sealing as above directed.*—The usual practice in employing the above method has been to expel air before sealing by introducing a few crystals or lumps of an alkali carbonate or bicarbonate, the gas set free on their contact with the acid being supposed to effectively expel all air. That this is not accomplished the following series of comparative results, long since published elsewhere,² fully shows. The material used was the oxide of uranium U_3O_8 , requiring by theory 32.07 per cent of UO_2 . Operating as just described on from 0.3 to 0.5 gram, the results were

31.06, 31.07, 29.72, 29.33, 29.89, 30.69,

whereas after filling the tube with gas from a generator there was found

32.11, 31.90, 32.15, 32.12, 32.06, 32.17, 32.28,

the average error of the former series being 1.78 per cent. The percentage error would, of course, be reduced by increasing the weight of mineral operated on. An average error equal to the above when employing 1 gram of ferrous minerals would make the percentage for FeO about 0.3 per cent too low. While the absolute error might be the same in all cases, the relative error would increase with minerals low in ferrous iron.

D. THE HYDROFLUORIC-ACID METHOD.

a. PRINCIPLE OF THE METHOD.

The hydrofluoric-acid method consists simply in securing complete decomposition of the powder in absence of air by means of hydrofluoric acid in presence of sulphuric acid, and titrating the ferrous iron in the resulting solution. It is the one which has been used almost exclusively in the Survey laboratories. The form of apparatus employed for a long time was the original one devised by J. P. Cooke³ (fig. 19, p. 205). But the method as ordinarily carried out is subject to

¹ Ullman, C., *Zeitschr. angew. Chemie*, 1893, p. 274; *Zeitschr. anal. Chemie*, vol. 33, 1894, p. 582.

² Bull. U. S. Geol. Survey No. 78, 1891, p. 50; *Chem. News*, vol. 64, 1891, p. 232.

³ *Am. Jour. Sci.*, 2d ser., vol. 44, 1867, p. 347.

two defects of opposite sign but unequal value, the second and greater of which long remained unsuspected.¹

It is possible to titrate ferrous iron in presence of sulphuric acid and as much as 5 to 7 cm.³ of 40 per cent hydrofluoric acid in a total volume of 200 to 400 cm.³ almost if not quite as exactly as in sulphuric acid alone, provided the iron solution is diluted with air-free water and the titration is made immediately after adding the hydrofluoric acid and with all possible dispatch. This condition can not be fulfilled in practice, because the mineral must be in contact with the acid for a long time in the apparatus commonly employed, and it seems to be almost impossible to prevent some oxidation during this period.

b. DEFECTS OF THE METHOD.

a. Oxidizability of divalent manganese by permanganate in the presence of hydrofluoric acid.—Manganic fluoride in dilute solutions is hardly at all dissociated, wherein it differs from manganic sulphate. The entering of the manganic ion as fast as formed into the undissociated state or into a complex ion² explains the fact that in the presence of hydrofluoric acid divalent manganese is oxidized readily by permanganate, whereby a sharp end reaction is rendered unattainable in the presence of much hydrofluoric acid, say over 7 cm.³ of 40 per cent acid. It is easy to obtain a transitory pink color throughout the liquid, but this disappears rapidly, the more rapidly the greater the amount of hydrofluoric acid or of manganous salt present. The oxidizer can be added by the cubic centimeter to solutions already containing manganous sulphate in presence of hydrofluoric acid without producing a more than passing pink color. The solution, however, takes on in ever-increasing intensity the red-brown color characteristic of manganic salts. Hence the decolorization due to this cause is much more pronounced in the case of rocks high in ferrous iron than in that of those low in this constituent, because of the greater amount of manganous salt resulting from reduction of a correspondingly larger amount of permanganate, and is also greater with increasing hydrofluoric acid. In presence of but little ferrous iron, up to say, 2 centigrams, and 5 to 7 cm.³ of hydrofluoric acid the color produced by a drop of permanganate lasts some time, but is very evanescent as the ferrous iron, and consequently the manganous salt formed, increases.

¹ It is not clear what, if any, bearing certain observations of E. Deussen (Monatsh. Chemie, vol. 28, 1907, p. 163) may have on the method. He claims that dissolving ferric oxide in hydrofluoric acid involves partial reduction of the iron with formation of both ferrous iron and hydrogen peroxide: $2\text{Fe}_2\text{O}_3 + 8\text{HF} = \text{Fe}_3\text{F}_8 + \text{FeO} + 3\text{H}_2\text{O} + \text{H}_2\text{O}_2$. The experiments described on the following pages do not indicate such action, at least in presence of sulphuric acid.

² Müller, E., and Koppe, P., Zeitschr. anorg. Chemie, vol. 68, 1911, p. 160.

E. Deussen,¹ on the basis of but a few tests, ascribes the extra consumption of permanganate to some obscure action of iron and seeks to counteract it by the addition of manganous sulphate. In both these assumptions he is, however, certainly in error,² as shown (1) by the fact that the addition of a drop or two of the oxidizer to a solution of ferric sulphate in even a large amount of hydrofluoric acid produces a very stable coloration, which is destroyed by the addition of manganous sulphate, and (2) by the above-mentioned very evident partial reoxidation of the reduced manganese. This last, the oxidation of divalent manganese by permanganate in the presence of hydrofluoric acid, can be effected with the greatest ease in the entire absence of ferric iron.

M. Dittrich and A. Leonhard,³ on the basis of numerous series of unconvincing tests, ascribed the indefinite end point to the effect of Ti_2O_3 . They slighted or ignored the demonstrated fact that in hydrofluoric acid solution divalent manganese is oxidized by permanganate, even quantitatively under proper conditions (11. D, p. 139), and that the simultaneous existence of trivalent titanium and trivalent iron in acid solution is not in accord with observation, for the former is oxidized easily by the latter, the reaction being used as the basis for titrating trivalent iron (9. D, p. 123). Hence, even if trivalent titanium occurs in some rock-forming minerals, it would be converted on solution to the quadrivalent state at the expense of ferric iron, and the ultimate titration by permanganate would involve only ferrous iron. Further, it is a fact that when much ferrous iron is titrated permanganate can be added without the attainment of a definite end point in amount far exceeding that which the titanium (if present as Ti_2O_3) would require.

Numerous tests have been made to ascertain the error due to oxidation of the manganese under conditions similar in respect to the amounts of iron involved to those encountered in rock analysis. Increasing amounts of hydrofluoric acid were added to fixed amounts of ferrous sulphate and sulphuric acid and the titration was made with the least possible expenditure of time. With not more than 7 cm.³ of 40 per cent hydrofluoric acid a very slight tendency was observed toward high results, but in most cases the results were identical with those obtained in the presence of sulphuric acid alone. As the amount of hydrofluoric acid was increased to 10 cm.³ a perceptible increase was noticed, which became markedly greater with 15 cm.³ of the acid, amounting in this case to about 0.2 cm.³ in the average on a normal consumption of 20 cm.³ of permanganate of 0.0032 FeO

¹ Zeitschr. anorg. Chemie, vol. 44, 1905, p. 425. See also Monatsh. Chemie, vol. 28, 1907, p. 163.

² This statement is confirmed by the work of O. L. Barnebey (Jour. Am. Chem. Soc., vol. 37, 1915, p. 1481).

³ Zeitschr. anorg. Chemie, vol. 74, 1912, p. 21.

titer. The personal factor enters here, G. Steiger having found slightly greater differences, but it is possible that they resulted from his titrating in more concentrated solutions, for with greater dilutions the differences are unquestionably less, according to experiments of my own.

Hence, after decomposition of the rock, removal of the excess of hydrofluoric acid is called for if the best results are to be expected. To a certain extent Treadwell's apparatus accomplishes this, but, as the experiments show, its complete expulsion is unnecessary.

A distinct contribution to the subject was made when O. L. Barnebey¹ investigated the effect of a large number of proposed preventives and found that boric acid is the most effective of all. When added, either as solid or in solution, it renders the fluorine inactive by formation of fluorboric acid (HBF_4), "which does not dissociate appreciably to yield hydrofluoric acid in the presence of boric acid."

β. *Extreme oxidizability of divalent iron by free oxygen in the presence of hydrofluoric acid or a fluoride.*—In comparing two series of results obtained with the Cooke apparatus, using a solution of ferrous sulphate in sulphuric acid alone in the one and in sulphuric acid with hydrofluoric acid in the other, a minus error was in all cases observed when the latter acid was present. An observation made by R. Peters,² but not applied by him to the present case, explains this. Ferric fluoride, like the corresponding manganic salt, is almost undissociated in solution, whereas the sulphate undergoes considerable dissociation, and in this state counteracts, to a great extent, the tendency of any ferrous iron present to become oxidized by free oxygen. Hence the slow oxidation of divalent iron by air in sulphuric-acid solution and its very rapid oxidation in the presence of hydrofluoric acid. While a sulphuric solution of ferrous sulphate exposed to the air in an open dish will hardly change in strength during an hour, a similar solution to which hydrofluoric acid has been added will suffer a large measure of oxidation in a quarter of the time. The change in titer becomes pronounced after a few minutes.

In the experiments with the Cooke apparatus referred to, the minus error should amount to not more than 0.1 to 0.2 cm.³ of permanganate on a normal consumption of 20 cm.³ or 0.5 to 1 per cent of the iron, but it may be considerably greater if the utmost care is not taken to employ carbon dioxide as free as possible from air and to exclude most carefully the entrance otherwise of air into the apparatus. It will also be greater the higher the concentration, within certain limits, of the solution during titration.

¹ Jour. Am. Chem. Soc., vol. 37, 1915, p. 1481.

² Zeitschr. physikal. Chemie, vol. 26, 1898, p. 193.

With a view to lessening the error, if possible, the mode of operating was varied by doing away with carbon dioxide, except at the start, shutting it off as soon as the bath was in active ebullition, and transferring the crucible direct from the hot bath to the titration vessel. The results were, if anything, a trifle better. As the employment of either the Cooke, Barnebey, or Treadwell apparatus involves long contact of the mineral with the acids, and as the experiments last mentioned were favorable in their results, it seemed as if the simple method of J. H. Pratt¹ might be modified in the same sense. He avoided the use of all apparatus other than a capacious platinum crucible fitted with a perforated cover for the introduction of carbon dioxide, in which he boiled the mineral powder with sulphuric and hydrofluoric acids, the decomposition being greatly hastened by the active movement and higher temperature and usually completed in five to ten minutes. The modification consists in doing away altogether with carbon dioxide, except at the start, and depending on the steam of the boiling iron solution to exclude air, a modification which Pratt himself tried with rather considerable minus errors, resulting perhaps from his having a smaller crucible at command than the method really demands. With a crucible of 100 cm.³ capacity, the following results with ferrous sulphate show what are the possibilities of the method:

Ferrous-iron determinations by the modified Pratt method.

[Strength of permanganate 0.0032 FeO per cm.³]

Time of boiling.	Permanganate used.	Normal consumption of permanganate.	Time of boiling.	Permanganate used.	Normal consumption of permanganate.
<i>Minutes.</i>	<i>cm.³</i>	<i>cm.³</i>	<i>Minutes.</i>	<i>cm.³</i>	<i>cm.³</i>
10	4.9	4.8	10	19.4	19.2
10	4.8	4.8	10	19.3	19.2
10	5.0	4.8	15	19.25	19.2
10	4.9	4.8	15	19.1	19.2
10	9.6	9.6	15	19.3	19.2
10	9.6	9.6	20	19.2	19.2
10	9.6	9.6	20	19.3	19.2
10	19.2	19.2			

These results leave little, if anything, to be desired. They show either normal values or a slight plus error instead of the invariable negative one of all previous determinations. The method was tested during two years in comparison with that of Cooke with favorable results, a few of which are shown in the table under A, page 190. It is the method employed by me in preference, not only because of its simplicity and quickness, but also because with it a coarser powder can be decomposed than with either the Cooke, the Barnebey, or the Treadwell method. However, as the exigencies of the FeO deter-

¹ Am. Jour. Sci., 3d ser., vol. 48, 1894, p. 149.

mination are now known to demand a powder as coarse as possible, a longer treatment has to be given than was called for by the fine powders used by Pratt.¹

C. INFLUENCE OF SULPHIDES, VANADIUM, AND CARBONACEOUS MATTER ON THE DETERMINATION OF FERROUS IRON BY THE HYDROFLUORIC-ACID METHOD.

A dark color of the insoluble fluorides and silicofluorides may be due to pyrite, graphite, or carbonaceous matter. The first of these affects the result but little, the second probably not at all, and they can be distinguished by their behavior toward nitric acid. Organic matter, of course, renders impossible the determination of ferrous iron.

α. Sulphides.—Pyrite, in the quantities usually met with in igneous rocks, is probably without serious effect on the ferrous-iron determination by any of the hydrofluoric-acid methods. This sulphide is very resistant toward attack in the absence of oxygen, as is shown by the fact that if present in any quantity it can be recognized readily in the residue after titration. In any case it is impossible to allow for an error introduced by its possible decomposition, and the result of titration must count as ferrous iron. In the case of soluble sulphides two sources of error are introduced—that of reduction of ferric iron by hydrogen sulphide evolved, and that due to the ferrous iron which the sulphides themselves may contain, especially if pyrrhotite is present. The first of these is perhaps negligible, for most of the hydrogen sulphide would probably be expelled without reducing iron. The second is approximately measurable if it is known that pyrrhotite is the only soluble sulphide present, and its amount has been ascertained by determining the hydrogen sulphide set free on boiling with hydrochloric acid in a current of carbon dioxide. In this case a correction is to be applied to the result of titration for total ferrous iron. (See also 26. C. b, p. 233, under "Sulphur.")

In order to obtain quantitative data regarding the effect of pyrite on the ferrous-iron determination by the hydrofluoric-acid method the following tests were made: Part of a fine crystal of pyrite was powdered rather finely and boiled with dilute sulphuric acid, which extracted considerable ferrous iron, derived presumably from admixed or intergrown pyrrhotite, as a second boiling with fresh acid gave a negative test for ferrous iron. After washing by decantation with water, followed by alcohol and ether, the powder was dried and further pulverized. A quarter of a gram of it when treated with hydrofluoric and sulphuric acids in a large crucible by the Cooke

¹ M. Dittrich (Ber. Deutsch. chem. Gesell., vol. 44, 1911, p. 990) facilitates the attack of refractory minerals by adding half a gram of not too finely ground quartz (not precipitated silica). The effect is to separate the mineral grains and prevent caking on the bottom of the crucible, thus exposing them to more effective action of the acid.



method for ferrous iron, then rapidly filtered through a very large perforated platinum cone fitted with filter paper, required but 2 drops of a permanganate solution representing only 0.0032 gram FeO to the cubic centimeter.

However, as H. N. Stokes found¹ that the oxidizing effect of ferric salts on pyrite and other sulphides is vastly greater than seems to have been suspected (see pp. 193-194), the following tests were made in order to ascertain the probable error due to this action under the conditions prevailing in rock analysis: Successive portions of 1 gram each of a hornblende schist, free from sulphur and carrying 10.09 per cent FeO as the mean of several determinations and 4.00 per cent Fe_2O_3 , were mixed in a large 100 cm.³ platinum crucible with 0.02, 0.025, and 0.10 gram, respectively, of the above purified pyrite powder, and treated with hydrofluoric and sulphuric acids by the Cooke method, the water bath being at boiling heat for one hour. The cooled contents of the crucible were poured into a platinum dish containing water and titrated rapidly nearly to an end. Then, in order to get rid of the pyrite, which would obscure the end reaction by its reducing effect on the permanganate, the solution was filtered as above and in the clear filtrate the titration was carried to completion. The results were 10.02, 10.16, and 10.70. Inasmuch as the smallest of these three charges of pyrite was several times greater than what may be considered an unusually high amount for an igneous rock, it is very evident that for all practical purposes the influence of pyrite on the ferrous determination by the Cooke method is negligible. At the same time it is to be borne in mind that with increased content in ferric iron an increased amount of pyrite will be attacked, and that the extent of this attack is influenced by the degree of fineness of the pyrite powder, which itself undergoes oxidation during grinding.

β . *Vanadium*.—If vanadium, when present, exists in the trivalent condition, it affects with an error varying with its amount the result of titration for ferrous iron. If the amount of the trivalent vanadium is known, a correction can be applied as follows: One molecule of V_2O_3 (150.8) in oxidizing to V_2O_5 requires as much oxygen as four molecules of FeO (288) when oxidized to Fe_2O_3 . The proportion, $150.8:288::\text{V}_2\text{O}_3 \text{ present}:x$, therefore gives the figure to be deducted from the uncorrected value for FeO. That this correction is very needful with many of the basic rocks becomes evident at once from the following perhaps extreme example:

Found 2.50 per cent apparent FeO in a rock containing .13 per cent V_2O_3 .

Deduct .25 per cent FeO equivalent in its action on KMnO_4 to .13 V_2O_3 .

Leaving 2.25 per cent FeO corrected.

¹ Bull. U. S. Geol. Survey No. 186, 1901; Am. Jour. Sci., 4th ser., vol. 12, 1901, p. 414.



Found 5.00 per cent apparent total iron as FeO_3 in the same rock.

Deduct .14 per cent Fe_2O_3 corresponding to .13 per cent V_2O_5 .

Leaving 4.86 per cent corrected total iron as Fe_2O_3 .

Deduct 2.50 per cent Fe_2O_3 equivalent to 2.25 per cent FeO .

Leaving 2.36 per cent Fe_2O_3 in the rock.

Failure to correct for the vanadium in both cases would have made the figures for FeO and Fe_2O_3 , respectively, 2.50 and 2.22 instead of 2.25 and 2.36 as shown above.

γ. Carbonaceous matter.—As said before (c, p. 201), matter of organic origin other than graphitic carbon renders the results of the ferrous-iron determination altogether unreliable.

d. THE METHOD IN ITS VARIOUS MODIFICATIONS.

α. According to Pratt (modified).—One-half to 1 gram of the coarsest powder¹ that can be used successfully is placed in a platinum crucible of 80 to 100 cm.³ capacity with a little air-free water and about 10 cm.³ of dilute sulphuric acid (1 acid to 3 water by volume). If the rock contains carbonates there will be effervescence, hence the acid must be added cautiously and the cover placed on till the action is over. There need be no fear of oxidation of ferrous iron at this stage, should any go into solution. Air-free hot water is now added till the crucible is at least half full; the crucible with cover on is placed on a triangle well down over a lamp turned low and protected from drafts. The air in the crucible is displaced rapidly by carbon dioxide entering beneath the lid slightly raised on one side. In a few seconds the liquid boils, but before allowing this to happen the gas current is stopped and the well-fitting lid lowered. Then from a small platinum crucible a measured quantity of strong hydrofluoric acid (5 to 7 cm.³) is poured in with one hand, while the other draws the lid a little to one side. A second of time suffices. The lid is replaced, the flame is increased for a few moments with great caution not to allow boiling over, and the moment steam is seen to issue around the lid it is again lowered to a point that causes steady ebullition without danger of loss. Steam should issue continually for five, ten, or as many minutes as may be deemed necessary or allowable. Then the crucible, still covered, is transferred with the tongs shown in figure 1 (p. 32) to the titration vessel, which may be of glass (containing a cold saturated solution of boric acid² in freshly boiled water with an excess of the solid acid and a few cubic centimeters of sulphuric acid) and which is already under the burette; the contents of the crucible are poured in quickly with the

¹ The fineness of grinding will depend on the nature of the rock. Most granite rocks require but moderately fine grinding, those high in ferruginous and refractory minerals generally, as tourmaline, need to be very fine.

² Barnebey, O. L., Jour. Am. Chem. Soc., vol. 37, 1915, p. 1481.

rinsings, and permanganate is run in rapidly till the first pink blush appears throughout the whole liquid.

Even without boric acid and with little iron the color will last some time, but with increasing amounts of iron, as also with increasing amounts of hydrofluoric acid, it fades with ever greater rapidity. In making a duplicate determination it is well to run in a little less than the calculated amount of permanganate before introducing the contents of the crucible.

The method should be tested first by the novice with ferrous-sulphate solution that has been standardized without hydrofluoric acid. It is important not to prolong the boiling unduly, for salts not easily soluble will separate, and as the temperature rises the oxidizing action of the concentrating sulphuric acid comes into play.

If an unattacked residue shows after titrating, this should be allowed to settle completely, then freed from the liquid by a decantation with water, once repeated. It is now transferred by a jet of water to a small agate mortar, allowed to settle again, freed from most of the water by decantation, ground for a few minutes under the water that remains, and washed back into the large crucible. The treatment with hydrofluoric and sulphuric acids, in smaller amounts and for a shorter time than at first, is then to be repeated. The succeeding titration can be made in the crucible itself after quickly filling this nearly full of cold air-free water. Usually decomposition will now be complete; if not, the various operations are to be repeated. In the very short time required for grinding the residues under water no appreciable oxidation of ferrous iron need be feared.

The directions given by Pratt¹ with reference to the treatment of a possible undissolved residue of very refractory minerals must be understood as applying only to homogeneous minerals and not to rocks, where the relations of ferrous and ferric iron in the undecomposed portion are certainly different from those in the part dissolved.

β. *According to Cooke.*²—The apparatus, as shown in figure 19, consists of a small water bath of a single opening and covered with a glass funnel the stem of which has been cut off near the flare, resting in a troughlike depression of the specially made cover. Into this trough water constantly drops from a tubulated bottle, thus securing a perfect water joint and serving to keep the bath full by overflowing on the inside. For the more perfect exclusion of air it is best to use water that has been freshly boiled. Through a small metal pipe carbonic-acid gas flows into the bath under the cover, but above the surface of the water, and rising through notches in the edge of the opening of the cover fills the funnel and crucible. (See footnote 1 to 9. C. a, p. 120.)

¹ Am. Jour. Sci., 3d ser., vol. 48, 1894, p. 150.

² Idem, 2d ser., vol. 44, 1867, p. 347.

One-half to 1 gram of the powder is treated exactly as in α until any carbonates that may be present cease to effervesce. The cover of the crucible is rinsed if need be and the open crucible at once placed in the opening of the bath, the funnel put in place, the gas current started, as also the flow of water from the reservoir, and the lamp under the bath already full of water is lit. As soon as it can

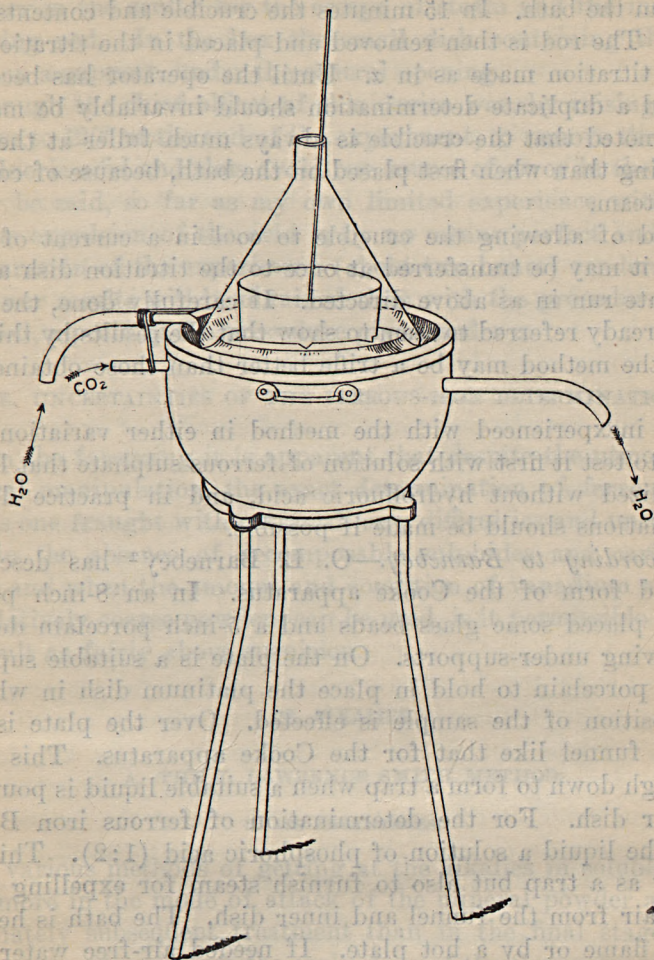


FIGURE 19.—Cooke's apparatus for ferrous-iron determination.

be safely assumed that the air in both funnel and crucible has been displaced a measured volume of strong hydrofluoric acid (5 to 7 cm.³) is poured into the crucible through a funnel of platinum or rubber and a platinum stirring rod is inserted through the stem of the glass funnel into the crucible. In the absence of a suitable funnel for the acid, the glass may be momentarily raised for the introduction of the acid, but not before the crucible has become filled with carbon dioxide.

When steam issues strongly from the funnel, the gas current from the generator is stopped and the apparatus left to itself for an hour, except for occasional stirring of the powder. When no gritty matter can be felt longer or when experience tells that decomposition must be complete, the gas current is turned on again, the lamp extinguished, and the water flow increased to the capacity of the outlet tube from the bath. In 15 minutes the crucible and contents should be cool. The rod is then removed and placed in the titration vessel and the titration made as in α . Until the operator has become experienced a duplicate determination should invariably be made. It is to be noted that the crucible is always much fuller at the end of the heating than when first placed on the bath, because of condensation of steam.

Instead of allowing the crucible to cool in a current of carbon dioxide, it may be transferred at once to the titration dish and permanganate run in as above directed. If carefully done, the experiments already referred to seem to show that the results by this variation of the method may be a trifle better than those obtained after cooling.

Those inexperienced with the method in either variation should not fail to test it first with solution of ferrous sulphate that has been standardized without hydrofluoric acid, and in practice duplicate determinations should be made if possible.

γ . *According to Barnebey.*—O. L. Barnebey¹ has described a simplified form of the Cooke apparatus. In an 8-inch porcelain dish are placed some glass beads and a 5-inch porcelain desiccator plate having under-supports. On the plate is a suitable support of glass or porcelain to hold in place the platinum dish in which the decomposition of the sample is effected. Over the plate is placed a 6-inch funnel like that for the Cooke apparatus. This extends far enough down to form a trap when a suitable liquid is poured into the outer dish. For the determination of ferrous iron Barnebey uses as the liquid a solution of phosphoric acid (1:2). This serves not only as a trap but also to furnish steam for expelling and excluding air from the funnel and inner dish. The bath is heated by a direct flame or by a hot plate. If needed air-free water can be added to replace that which evaporates, by the aid of a platinum rod. Reference to the description of the Cooke apparatus renders further explanation unnecessary.

Of course, the absence of provision for introducing carbon dioxide makes it necessary to transfer the hot solution of the sample to the titration vessel, and the need of a fine powder is a serious objection, as with the Cooke apparatus. The latter has the advantage over

¹ Jour. Am. Chem. Soc., vol. 33, 1916, p. 374.

Barnebey's modification that the introduced carbon dioxide effects more rapid expulsion of the air in the decomposition vessel than is possible by the aid of steam alone.

8. *According to Treadwell*.—F. P. Treadwell¹ used a paraffin bath in which was supported a lead box having a lead cover provided with two openings, one at the side for introducing carbon dioxide, the other in the center for the escape of steam and the insertion of a stirring rod. In the box the small dish containing the sample rested on a support, under the central opening.

Although the chief object of this device was, by raising the temperature to 120° at the end of the experiment, to remove the excess of hydrofluoric acid and thus avoid one source of error in the titration, it may be said, so far as my own limited experience with it goes, that the expulsion of the acid is by no means perfect and that the long duration of the experiment (about two hours) renders it likely that lower results will be obtained than with the procedures already described, especially the procedure given under *a*.

E. UNCERTAINTIES OF THE FERROUS-IRON DETERMINATION.

From the foregoing it is apparent that despite the utmost care in practical manipulation, the exact determination of ferrous iron in rocks is one fraught with extraordinary difficulties and uncertainties. Only in the absence of decomposable sulphides and carbonaceous matter and when the amount and condition of vanadium are known and relatively coarse powders can be used, is it permissible to regard the result as fairly above suspicion.

22. ALKALIES.

A. THE J. LAWRENCE SMITH METHOD.

B. ITS ADVANTAGES.

The various methods of getting at the alkalies in soluble silicates differ more in the mode of attack of the mineral powder and in the immediately subsequent treatment than in the final stages. With very few exceptions, since the early days of the Survey's existence all alkali determinations have been made by the method of J. Lawrence Smith,² which is far more convenient than and fully as accurate as those in which decomposition is effected by hydrofluoric and sulphuric acids, or by bismuth, lead, or boric oxides. One of its chief advantages is the entire elimination of magnesia at the start.

¹ Kurzes Lehrbuch der analytischen Chemie, 6th ed., 1913, vol. 2, p. 425.

² Am. Jour. Sci. 2d ser., vol. 50, 1871, p. 269; Am. Chemist, vol. 1, 1871; Annalen Chem. und Pharm., vol. 159, 1871, p. 82.

D. REAGENTS AND APPARATUS.

Decomposition of the powder is effected by heating it with its own weight of ammonium chloride and eight times as much precipitated calcium carbonate.

The ammonium chloride used must be purified, preferably by sublimation, or made by neutralizing pure ammonia by pure hydrochloric acid, and the calcium carbonate is obtained best from pure calcite by solution and precipitation. However obtained, this last is rarely free from alkalis, which must be estimated once for all in a blank test in order to apply a correction. Eight grams of the carbonate will yield usually from 0.0012 to 0.0016 gram of alkali chlorides, almost entirely the sodium salt, but the amount has been brought down to half the above by very long washing. This correction may be admitted at once to be a defect of the method, but it is one easily applied with safety. It is not at all certain that all the alkali found in the blank test comes from the carbonate. Much hot water is used for the analysis and a hot-water bottle, even of the best glass, will afford weighable amounts of alkali.

The ignition may be made in a covered crucible of ordinary shape and of about 20 to 30 cm.³ capacity, heated to full redness for not more than two-fifths of its height, but the heat has to be kept so low in this case to avoid loss by volatilization that perfect decomposition is not always assured.¹ Hence, to avoid waste of time in very fine grinding, the form of crucible with cap originally advocated by Smith is very much to be preferred, since it permits, when set at an angle through an opening in the side of a fire-clay cylinder, the application of the full heat of two burners, and perfect decomposition invariably results without the need of extraordinary care in grinding. The crucible used in the Survey laboratory (fig. 20) for one-half gram of rock powder and 4 grams of calcium carbonate is 8 cm. long, 1.8 cm. wide at the mouth, and 1.5 cm. at the bottom. For double the amounts or more the dimensions are 8 cm., 2.5 cm., and 2.2 cm. The weights are 25 and 40 grams.

C. TREATMENT OF THE MINERAL POWDER.

Perfectly satisfactory results are to be obtained with but half a gram of rock powder. This is weighed out, ground fine in a large agate mortar, mixed with its own weight of sublimed ammonium

¹ R. L. Steinlen (Chem. Zeitung, vol. 29, 1905, p. 364) describes a simple cooler for the lid of an ordinary crucible to obviate this difficulty. E. W. Morley (private communication) uses with good effect as a lid a closely fitting small platinum dish filled with cold water. Th. Döring (Zeitschr. anal. Chemie, vol. 49, 1910, p. 158) in a careful test of the method found that an ordinary crucible gave excellent results if it was set in a hole in asbestos board. After the preliminary gentle heating the full heat of a Teclu burner could be applied without loss of alkali. E. Wilke-Dörfurt confirms this finding (Zeitschr. anal. Chemie, vol. 51, 1912, p. 755).

chloride, and the two are ground together thoroughly. Then nearly all of 4 grams of calcium carbonate is added and the grinding continued till a thorough mixing has resulted. The contents of the mortar are transferred to the long crucible, the rest of the carbonate being used for rinsing off mortar and pestle. The crucible is then capped and placed in an inclined position in a clay cylinder (fig. 20) or through a hole in a piece of stout asbestos board clamped in a vertical position, and heated for about ten minutes by a low flame placed at considerable distance beneath. As soon as the odor of ammonia is no longer perceptible the nearly full flame of two Bunsen burners is substituted, and continued for 40 to 50 minutes. The sintered cake¹ detaches readily from the crucible as a rule; if not, it is softened up in a few minutes by hot water and digested in a dish until thoroughly disintegrated. It is first washed by decantation, and any lumps are broken up by a pestle, then thrown on the filter and well washed with hot water. The residue should dissolve completely in hydrochloric acid without showing the least trace of unattacked mineral, not even of quartz, though sometimes a few black particles of iron ores will dissolve but slowly.

Inasmuch as J. W. Mellor² and M. Dittrich³ report 0.1 to 0.2 per cent of the alkali, and M. F. Connor⁴ even more, as not recovered by one treatment according to Smith, it may be necessary when the alkali content is considerable to dry and reheat the extracted mass with calcium carbonate and ammonium chloride and to add the second extract to the first. The unfavorable results reported may have been due to an insufficient temperature.

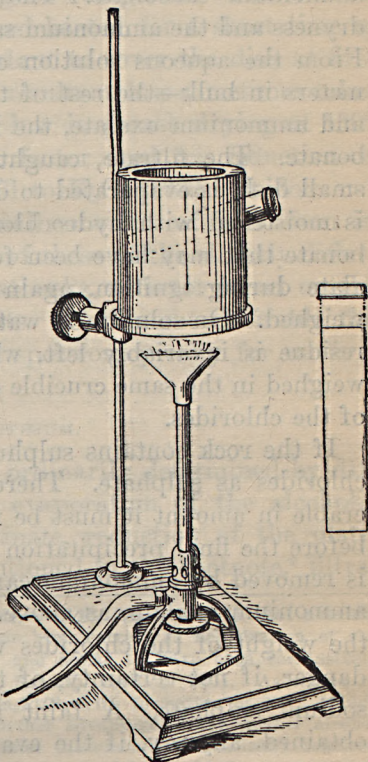


FIGURE 20.—The J. Lawrence Smith crucible for alkali determinations. For dimensions see text.

¹ To avoid the formation of a melted cake with silicates high in iron it is advisable to increase the proportion of calcium carbonate. In order to lessen the chance of adhesion to the bottom W. T. Schaller, of the Survey laboratory, finds it well to place a layer of calcium carbonate at the bottom of the crucible before introducing the mixture. George Steiger finds that the slacking of the cake is aided by using but 1 or 2 cm.³ of water at first.

² Quantitative inorganic analysis, pp. 225, 247.

³ Neues Jahrb., 1903, vol. 2, p. 69.

⁴ Cong. géol. internat., 12^e sess., Canada, 1913, p. 885.

E. Mäkinen¹ uses calcium chloride (melted and kept in a well-stoppered bottle) instead of the mixture of calcium carbonate and ammonium chloride and claims to get with it a slightly more perfect attack in consequence of the fusion which accompanies its use. Naturally the flux must be tested for an alkali content.

D. SEPARATION OF CALCIUM AND SULPHURIC ACID.

All but a trifling amount of the calcium is separated at boiling heat in a large platinum dish by double precipitation by ammonia and ammonium carbonate. The combined filtrates are evaporated to dryness and the ammonium salts are carefully driven off (B, p. 33). From the aqueous solution of the residue—but a few cubic centimeters in bulk—the rest of the calcium is thrown out by ammonia and ammonium oxalate, the last being more effective than the carbonate. The filtrate, caught in an untared platinum crucible or small dish, is evaporated to dryness and gently ignited; the residue is moistened with hydrochloric acid to decompose any alkali carbonate that may have been formed by action of the ammonium oxalate during ignition, again evaporated, ignited very gently, and weighed. On solution in water a few tenths of a milligram of fixed residue is invariably left, which should be collected, ignited, and weighed in the same crucible or dish in order to arrive at the weight of the chlorides.

If the rock contains sulphur, this will be found in part with the chlorides as sulphate. Therefore, if the sulphur is at all considerable in amount it must be removed by a drop of barium chloride before the final precipitation of the calcium. The excess of barium is removed by ammonium carbonate and the last of the calcium by ammonium oxalate, as above. If the sulphur is not thus removed, the weight of the chlorides will be slightly in excess, and there is danger, if not certainty, of the potassium chloroplatinate carrying sodium sulphate. A faint reaction for sulphate can usually be obtained, anyway, if the evaporations have been made on a water bath heated by gas.

E. PRECIPITATION OF POTASSIUM.

To the solution of the chlorides in a small porcelain dish² there is added sufficient chlorplatinic acid solution (containing 10 per cent of platinum) to react with both the sodium and potassium. The dilution should be such that when heated on the water bath any precipitate that may form redissolves wholly. This is to prevent

¹ Zeitschr. anorg. Chemie, vol. 74, 1912, p. 74.

² Preferred to platinum because of the possibility, under certain rare and ill-understood conditions, of the formation of an insoluble platinum compound, probably by reaction between the platinum of the dish and that of the salt. (See also Bolm, F., Zeitschr. anal. Chemie, vol. 38, 1899, p. 349.)

occlusion of mother liquor in a mass of crystals suddenly formed. Evaporation is then carried on till the residue solidifies on cooling. It is then drenched with alcohol¹ of 80 per cent strength, filtered by decantation through a very small filter, and washed by decantation with alcohol of the same strength. The precipitate is not brought onto the filter more than can be avoided. Dish and filter are then dried for a few minutes to remove adhering alcohol, the contents of the former are transferred to a weighed platinum crucible or very small dish, and what still adheres to the porcelain is washed through the filter with hot water into the weighed receptacle. This is now placed on the steam bath and afterward heated for a short time to 135° in an air bath. It is very important to cover the dish at first in the air bath, for decrepitation with resultant loss sometimes takes place if this is not done. With rocks low in potash drying at 100° suffices fully to expel all water. The factor used for reduction of K_2PtCl_6 to $2KCl$ is 0.307 and of $2KCl$ to K_2O , 0.632. It does not seem necessary with the relatively small amounts of potassium in rocks to make use in place of the first of these of the slightly different empirical factor given in some textbooks, a factor based on the analysis of commercial potassium salts. If thought desirable the potassium chlorplatinate can be tested spectroscopically for caesium and rubidium.

1. SODIUM AND LITHIUM.

If it is desired to check the sodium, ordinarily determined by difference, this can be done readily by evaporation of the alcoholic filtrate from the potassium chlorplatinate, reduction of the platinum by hydrogen or otherwise as mentioned in the footnote,² filtra-

¹ The claim of H. Precht (Zeitschr. anal. Chemie, vol. 18, 1879, p. 513) that absolute alcohol is preferable, especially if evaporation has been carried to dehydration of the sodium salt, has been disputed by A. Atterberg and seems to have been conclusively disproved by J. Morozewicz (Anzeig. Akad. Wiss. Krakau, 1906, p. 796). According to Morozewicz, absolute alcohol partly decomposes Na_2PtCl_6 with formation of $NaCl$, which goes to increase the weight of the K_2PtCl_6 . A further advantage of the weaker alcohol lies in the fact that no more chlorplatinic acid than the amount theoretically required to convert both sodium and potassium to chlorplatينات need be used. In cases calling for the highest degree of accuracy Precht's solubility coefficient for K_2PtCl_6 in 80 per cent alcohol can be used, namely, 1:26400. H. Fresenius and P. H. M.-P. Brinton (Zeitschr. anal. Chemie, vol. 50, 1911, p. 21) after extended study adhere to the use of alcohol of 80 per cent strength.

² When haste is not an object, this way of Bunsen's for removing platinum from the chlorides of the alkalies is by far the neatest and most satisfactory. The small flask containing the solution is placed in a water bath and attached to a hydrogen generator. After expelling all air the flask is closed, without breaking connection with the generator, and left to itself, except for occasional light shaking up, till reduction is accomplished. A more expeditious and very satisfactory reduction is effected by evaporating the solution to dryness with metallic mercury, then heating to expulsion of the excess of mercury and of its chloride. E. Sonstadt (Jour. Chem. Soc., vol. 67, 1895, p. 984) thus reduces potassium chlorplatinate in order to weigh its platinum. M. Horsch (Compt. Rend., vol. 168, 1919, p. 167) effects reduction by heating the solution in a platinum dish on the steam bath with 2 to 3 cm.³ of alcohol. Contact with metallic platinum is essential. The deposit is adherent to the dish.

tion, evaporation, and weighing of the sodium chloride. A check made in this way should agree with the determination by difference within half a milligram on the weight of the chloride. Lithium may then be tested for by the spectroscope, or in case no direct weighing of the sodium chloride is made, the evaporated alcoholic solution may be examined directly. Lithium is almost invariably present, but almost never in amount to warrant quantitative estimation. Should it be so, however, the very excellent Gooch method (summarized below) of separation by amyl alcohol is to be followed. In rock analysis there need be no fear of enough lithium falling with the potassium to cause any concern.

If ammonium carbonate alone has been relied on to separate all calcium (see d, p. 210) the few tenths of a milligram of calcium chloride that escaped precipitation should be separated now from the sodium and the proper correction made.

a. Gooch's method¹ for separating lithium.—Gooch thus describes his method for separating lithium:

To the concentrated solution of the chlorides amyl alcohol is added and heat is applied, gently at first, to avoid danger of bumping, until the water disappearing from solution and the point of ebullition rising and becoming constant for some minutes at a temperature which is approximately that at which the alcohol boils by itself, the chlorides of sodium and potassium are deposited and lithium chloride is dehydrated and taken into solution. At this stage in the operation the liquid is cooled and a drop or two of strong hydrochloric acid added to reconvert traces of lithium hydrate in the deposit, and the boiling continued until the alcohol is again free from water. If the amount of lithium chloride present is small, it will now be found in solution and the chlorides of sodium and potassium will be in the residue, excepting the traces, for which correction will be made subsequently. If, however, the weight of lithium chloride present exceeds 10 or 20 mg., it is advisable at this point, though not absolutely essential to the attainment of fairly correct results, to decant the liquid from the residue, wash the latter a little with anhydrous amyl alcohol, dissolve in a few drops of water, and repeat the separation by boiling again in amyl alcohol. For washing, amyl alcohol, previously dehydrated by boiling, is to be used, and the filtrates are to be measured apart from the washings. In filtering it is best to make use of the perforated crucible and asbestos felt, and apply gentle pressure. The crucible and residue are ready for the balance after drying for a few minutes directly over a flame turned low. The weight of insoluble chlorides actually obtained in this manner is to be corrected by the addition of 0.00041 gram for every 10 cm.³ of amyl alcohol in the filtrate, exclusive of washings, if the insoluble salt is entirely sodium chloride, 0.00051 gram for every 10 cm.³ if potassium chloride constitutes the residue, and, if both sodium and potassium chlorides are present, 0.00092 gram; but * * * the entire correction may in any case be kept within very narrow limits if due care be given to the reduction of the volume of residual alcohol before filtration. The filtrate and washings are evaporated to dryness, treated with sulphuric acid, the excess of the

¹ Proc. Am. Acad. Arts and Sci., 1886, p. 177; Bull. U. S. Geol. Survey No. 42, 1887, pp. 85-86; Chem. News, vol. 55, 1887, pp. 18, 29, 40, 56, 78; Am. Chem. Jour., vol. 9, 1887, p. 33. Consult also Skinner, W. W., and Collins, W. D., Bull. Bur. Chemistry No. 153, 1912.

latter driven off, and the residue ignited to fusion and weighed. From the weight thus found the subtraction of 0.0005 gram is to be made if sodium chloride constitutes the precipitate, 0.00059 gram if potassium chloride alone is present in the residue, and 0.00109 gram if both these chlorides are present, for every 10 cm.³ of filtrate, exclusive of washings.

Amyl alcohol is not costly, the manipulations of the process are easy, and the only objectionable feature—the development of the fumes of amyl alcohol—is one which is insignificant when good ventilation is available.

The process has been used for some months frequently and successfully, by others as well as by myself, for the estimation of lithium in waters and minerals.

B. PRELIMINARY TREATMENT BY OTHER METHODS.

It may happen, for lack of sufficient material in the case of silicate minerals decomposable by hydrochloric acid, that it is necessary to determine the alkali as well as other bases and silica and titanium oxide in the same portion of the sample after all of these have been separated by methods which exclude the use of alkali reagents. Then the question of a suitable method for separating magnesium becomes important. Because of its cumbersomeness and possible sources of error the old barium-hydroxide method is not to be recommended in comparison with the methods that follow.

a. THE MERCURIC OXIDE METHOD.

The mercuric oxide method of Zimmermann, whereby the magnesia is precipitated from solution of the chlorides by moist, freshly precipitated, and alkali-free mercuric oxide, can give satisfactory results. The oxide is added in excess to the solution in a platinum crucible and evaporated to dryness. Then the mercuric chloride and most or all of the excess of oxide are expelled by cautious heating. On leaching with water the magnesia remains on the filter. With more than 1 per cent of magnesia the operation must be repeated (Dittrich).

b. THE AMMONIUM CARBONATE METHOD.

The once favored method of precipitating the magnesium by neutral ammonium carbonate in concentrated solution has been again recommended.¹ The magnesium solution must be as strongly concentrated as possible, and a great excess of ammonium carbonate solution must be used. A voluminous precipitate forms, which dissolves on vigorous stirring if enough of the precipitant is used. After a time a crystalline precipitate falls—a double carbonate of

¹ Wülfing, E. A., Ber. Deutsch. chem. Gesell., vol. 32, 1899, p. 2214. The neutral carbonate is prepared by dissolving 230 grams of ammonium carbonate in 180 cm.³ of ammonia of 0.92 specific gravity and enough water to make 1 liter. This is sometimes called Schaffgotsch's solution.

magnesium and ammonium—which is insoluble in the concentrated solution of ammonium carbonate. Allow to stand for six to twenty-four hours. Wash with the concentrated ammonium carbonate solution. It is no exercise of undue caution to redissolve and reprecipitate, to make sure of getting all alkali in the filtrate, especially potassium.

F. A. Gooch and E. A. Eddy¹ find that, when carried out as directed above by Wülfing, precipitation of the magnesium is incomplete, but that this defect can be remedied by addition of alcohol. Of several procedures devised they prefer the following as most convenient for the proportions of salts they used, namely, about 0.15 gram MgO and 0.1 to 0.2 gram alkali chlorides.

A solution is first prepared by saturating with ammonium carbonate a mixture in the proportions by volume of 18 cm.³ ammonia solution [density 0.92?], 80 cm.³ water and 90 cm.³ absolute alcohol. The solution containing the chlorides of magnesium and the alkalies is brought to a volume of about 50 cm.³ and an equal amount of absolute alcohol is added. Precipitation is made by addition of 50 cm.³ of the prepared reagent and the mixture is allowed to stand 20 minutes, with stirring for 5 minutes. If the amount of alkali salts originally present is small, the precipitate may be collected on asbestos in a perforated crucible and washed with the precipitant. When the amount of alkali salt originally present is large, the precipitate may be freed from traces of the alkali salt by pouring off the supernatant liquid through the prepared asbestos filter, dissolving the precipitate, and precipitating ammonium-magnesium carbonate as at first. If it is desired to determine the magnesium as well as the alkalies, the precipitate of carbonate freed from alkalies is ignited and the residual magnesium oxide weighed.

C. THE AMYL ALCOHOL METHOD.

Under certain circumstances, notably in the absence of lithium, the method of Gooch developed by Riggs² may be satisfactory. It is similar to that of Gooch for separating lithium from sodium and potassium chlorides by amyl alcohol, and involves the same solubility corrections for the alkali chlorides above noted (A. f. α , p. 212) in the description of Gooch's method.

C. DIRECT SEPARATION OF POTASSIUM BY SODIUM COBALTINITRITE.

It may happen sometimes that of the alkalies present the percentage of potassium alone is desired. In this case use may be made of

¹ Am. Jour. Sci., 4th ser., vol. 25, 1908, p. 444; Chem. News, vol. 97, 1908, p. 280.

² Am. Jour. Sci., 3d ser., vol. 44, 1892, p. 103.

the cobaltinitrite method, which afforded W. Autenrieth¹ results that are in good agreement with those obtained by the J. Lawrence Smith method.

A. PREPARATION OF THE REAGENT.

Crystallized cobalt nitrate (30 grams) is dissolved in 60 cm.³ of water. To the solution is added 100 cm.³ of a saturated solution of sodium nitrite (corresponding to 50 grams of NaNO₂) and 10 cm.³ of glacial acetic acid. Effervescence, with escape of nitric oxide, ensues and the color changes to dark yellow-brown. Some potassium cobaltinitrite usually separates, which, after one to two days, is filtered off. The reagent undergoes hardly any decomposition in three to four weeks if kept in a dark bottle. It is still available if a few drops, when added to 5 cm.³ of water containing one drop of 10 per cent KCl solution, cause almost immediately a yellow precipitation.

B. APPLICATION OF THE METHOD.

The mineral powder (1 to 3 grams) is decomposed with hydrofluoric and sulphuric acids, the excess of the sulphuric acid is volatilized, the dry residue is ground and digested with 30 to 40 cm.³ of water. To the solution, contained in a capacious beaker of Pyrex or Jena glass (or in a platinum dish), is added 10 cm.³ of a saturated solution of potassium-free sodium acetate² and the mixture is boiled for from 10 to 15 minutes. The precipitate of basic acetates is filtered and washed a few times with hot water. The filtrate is evaporated to a bulk of 15 to 20 cm.³, then, according to the amount of potassium present, 5 to 10 cm.³ of the cobalt reagent is added, and after stirring the liquid is let stand for 24 hours, cold. The yellow precipitate is filtered, washed with cold water containing a little of the reagent, and dried at 100°. As it is not free from sodium, it is useless to weigh it in this condition, and it is treated therefore as in α or β below.

R. C. Haff and E. H. Schwartz³ treat the filtrate obtained after attack according to Lawrence Smith, as follows:

An excess of acetic acid (5 to 10 cm.³) is added and evaporated till the odor of the acid is no longer perceptible. The residue is taken up with a little hot water, from 10 to 15 cm.³ of the cobalt reagent is added, and the solution is evaporated to a pasty consistency. After cooling, cold water (30 cm.³) is poured upon the residue, with care to wash the sides of the dish well. The solution is filtered and washed with water, which should be cold.

¹ Centralbl. Mineralogie, 1908, p. 513.

² Five grams dissolved in water should give no yellow precipitate with the cobalt reagent after 24 hours.

³ Jour. Ind. Eng. Chemistry, vol. 9, 1917, p. 785.

The further treatment differs according as the potassium is to be weighed as chlorplatinate or as perchlorate.

α. Determination as chlorplatinate.—The precipitate is removed from the paper, which is ashed in a platinum crucible; the precipitate is then added and heated to dull redness for a few minutes. The resulting alkali nitrites are extracted with hot water, filtered from the cobalt oxide, evaporated to dryness with strong hydrochloric acid, and the potassium is determined as in A. e, p. 210.

β. Determination as perchlorate.—The yellow precipitate is transferred as far as possible to a small porcelain dish, the paper is ashed and its aqueous extract is added to the contents of the dish. To this is then added, drop by drop, a few cubic centimeters of hydrochloric acid (sp. gr. 1.124), the blue solution is evaporated to complete dryness and treated with 5 to 6 cm.³ of perchloric acid (sp. gr. 1.124) free from sulphuric acid. The solution is evaporated to dryness, treated again with 6 cm.³ of perchloric acid, again evaporated to dryness, and finally heated over a free flame till copious vapors of perchloric acid come off. There must be complete conversion of the salts to perchlorates, and ammonium salts must be absent. The residue is then extracted with 10 cm.³ of absolute alcohol containing 0.2 per cent of perchloric acid and allowed to stand for some minutes. The clear solution is filtered through a platinum-felted crucible without disturbing the precipitate, which is transferred and washed with absolute alcohol saturated with potassium perchlorate¹ and containing 0.2 per cent of perchloric acid, dried at 120° to 130°, and weighed. It is not considered necessary to wash finally with alcohol and ether in order to remove the very small amount of wash liquid that adheres to the precipitate.

As applied when sodium is present the procedure is somewhat different. In that case the precipitate is transferred to the crucible by means of the filtrate,² washed once or twice with the alcoholic solution of perchloric acid, redissolved and reprecipitated, and finally washed with the alcoholic solution of perchlorate and perchloric acid.

¹ Davis, W. A., Jour. Agr. Sci., vol. 5, 1912, p. 52. Thin, R. G., and Cumming, A. C., Jour. Chem. Soc., vol. 107, pt. 1, 1915, p. 361. Baxter, G. P., and Kobayashi, M., Jour. Am. Chem. Soc., vol. 39, 1917, p. 249. The earlier directions, to use alcohol containing only perchloric acid, involve too great a solubility loss. Thin and Cumming prepare the solution by shaking up the alcohol and perchlorate for 10 minutes and pouring off the clear liquid. Baxter and Kobayashi use alcohol saturated at 0° and wash at the same temperature. The solution must be prepared shortly before use.

² Gooch, F. A., and Blake, G. R., Am. Jour. Sci., 4th ser., vol. 44, 1917, p. 381.

23. CARBON DIOXIDE, CARBON.

A. QUALITATIVE TEST FOR CARBON DIOXIDE.

In the preliminary qualitative test for carbon dioxide, it must be remembered that while calcite gives off its carbon dioxide on treatment with cold acid, dolomite and siderite do not, and hence warming should not be omitted; otherwise a few tenths per cent of carbon dioxide can be overlooked. Moreover, the powder should first be agitated with a little hot water, to remove all inclosed air which might otherwise be mistaken for carbon dioxide. In order not to overlook traces the test should be made in a test tube, first boiling the powder with a little water, then cooling, and adding dilute hydrochloric acid. If effervescence is immediate the presence of calcite is assured; if escape of bubbles takes place only on warming the carbonate is not calcite. In order to make sure of the reaction it may be necessary to use a pocket lens, holding the test tube in an inclined position and looking down in order better to see the minute bubbles as they stream up along the upper glass wall. It is, of course, important not to mistake escaping hydrogen sulphide for carbon dioxide.

B. QUANTITATIVE TEST FOR CARBON DIOXIDE.

For the quantitative determination of carbon dioxide an apparatus permanently set up is used, of which several forms have been described by different writers.¹ The one depicted in figure 21 is a compact arrangement long used in the Survey laboratory.

The rock powder (1 to 5 grams) is boiled with dilute hydrochloric acid in a small Erlenmeyer flask attached to an upward-inclined condenser, whence, after passing through a drying system—calcium chloride, anhydrous copper sulphate to retain hydrogen sulphide from decomposable sulphides and any hydrochloric acid that may pass over, then calcium chloride again—the carbon dioxide is caught by absorption tubes filled with soda lime followed by calcium chloride. Of course, arrangement is made for a current of air free from carbon dioxide with which to sweep out the apparatus before and after the determination and for a slow current during its continuance. The results are very accurate and the determination can be carried out quickly.

The manipulations are as follows: Hot water is poured upon the powder in the flask; this is attached to the condenser, and a current of air free from carbon dioxide is forced through the whole system, except the weighed absorption tubes, until the original air has been

¹ For a simple and convenient form, see Treadwell's "Quantitative analysis," 4th American ed., p. 381.

displaced, the observation bulbs E being attached directly to the drying system B. Then the stopcock in the separatory funnel is closed, the funnel is half filled with hydrochloric acid (1:1), the rubber stopper of the funnel is replaced, the absorption tubes are inserted between B and E, and the acid is allowed to flow into the

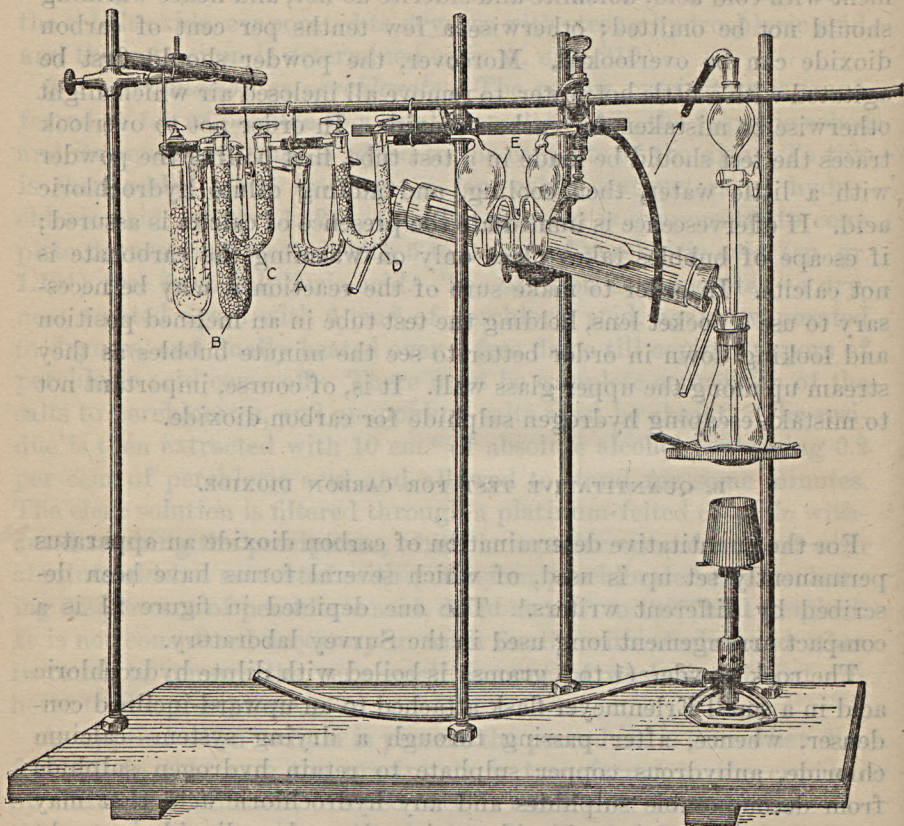


FIGURE 21.—Compact form of apparatus for determination of carbon dioxide. A, Protective calcium chloride tube, frequently refilled, to retain most of the moisture from the condenser. B, Double U-tube, filled in the center with pumice impregnated with anhydrous copper sulphate and at both ends with calcium chloride. C and D, Absorption tubes, C and one-third of D containing soda lime, followed in D by calcium chloride. C needs to be refilled before the soda lime in D has absorbed much if any carbon dioxide, D then requires only occasional refilling, but it will not do to use it indefinitely, since the calcium chloride in it becomes less and less effective as it takes up the water set free from the soda lime in C during its conversion to carbonate. E, Observation bulbs containing sulphuric acid to show the rate of gas flow.

flask, slowly if there is much carbon dioxide, rapidly if there is but little. When effervescence diminishes in the former case, at once in the latter, the lamp is lighted and the flow of water through the condenser started. The flame is kept low, so as to have steady but quiet ebullition, and the gas current is not interrupted, although

reduced to a slow rate. With much carbon dioxide the rate of absorption is noted very readily by holding the hand to the soda-lime tubes, which become hot or warm where absorption is taking place. A sufficient time having elapsed, the flame is extinguished and the air current increased. When cool the tubes C and D are weighed after remaining some time in the balance case.

The soda lime must be porous, not hard and unabsorptive like that sometimes used for the combustion of nitrogenous organic substances and should contain 2 per cent of water for the most effective absorption of carbon dioxide.

For the simultaneous determination of carbonates and the carbon of carbonaceous matter see C, below.

It has been shown already under "Water" (5. C. h, p. 89) how in case of need, as because of paucity of material, the determination of carbon dioxide can be combined with that of water by fusion with lead chromate, provided that free carbon or organic matter is absent. Soda-lime absorption tubes then follow the calcium chloride tube in carrying out the determinations there referred to.

L. H. Borgstrom¹ calls attention to the difficulty of decomposing by hydrochloric acid some minerals that contain carbon dioxide, especially certain scapolites. When these are present he adds to the hydrochloric acid 80 cm.³ of a mixture of 1 part strong hydrofluoric acid and 4 parts water. He recommends also to pass hydrochloric acid gas through the calcium chloride in the tubes B before use, in order to neutralize any alkalinity it may have and so prevent retention of some of the carbon dioxide by it.

C. CARBON.

Fusion with lead chromate is commonly resorted to in order to determine the carbon of graphite or carbonaceous matter in rocks and ores, though boiling in presence of sulphuric and chromic acids can be made to yield good results.

If carbonates are at the same time present they can be determined as in B (p. 217), and by a second determination, as just referred to, the total carbon in both forms can be found as CO₂, whence that of the graphite is derived by difference. Or, according to G. T. Morgan,² the carbonates are first decomposed as in B by orthophosphoric instead of hydrochloric acid, whereupon chromic acid is added and the carbon oxidized and determined as CO₂.

A. C. Fieldner, W. A. Selvig, and G. B. Taylor,³ in a recent paper, describe a procedure for determining the carbon and hydrogen of combustible matter in shales, clays, and limestones, which seems to

¹ Zeitschr. anal. Chemie, vol. 53, 1914, p. 685.

² Jour. Chem. Soc., vol. 85, 1904, p. 1001.

³ Bur. Mines Tech. Paper 212, 1919.

afford results as satisfactory as could be expected. It does not take account of volatile components of the combustible matter that might be driven off in the preliminary treatment of the rock.

24. CHLORINE.

A. CONDITION IN ROCKS.

Chlorine may exist in rocks in a water-soluble condition, in minerals that are decomposed by nitric acid, and in those not attacked by this acid. In the first form it doubtless exists as infiltrated sodium chloride or as original inclusions in one or more of the constituent minerals; in the second in minerals of the sodalite group and sometimes apatite; in the last chiefly in the scapolites. Where a qualitative test shows the water-soluble form to be present in determinable amount, it must be extracted separately and the amount found deducted from the total as determined in a second portion. Sometimes it may be possible to use the extracted material for the determination of the rest of the chlorine.

B. DETERMINATION OF WATER-SOLUBLE CHLORINE.

A suitable amount, which may be several grams, of the powder is extracted with water. Very often the filtrate is turbid, a condition which may sometimes be prevented by using double filters or by adding some chlorine-free salt, like sodium nitrate, to the wash water. If the filtrate remains persistently cloudy the precipitation of silver chloride may be proceeded with as usual, after acidifying with nitric acid. It is best to let the precipitate settle over night in order to obtain a clear filtrate on the morrow. It is collected on a small filter, washed with water acidified with nitric acid, dried, and ignited in a very small porcelain crucible without allowing the paper to burst into flame. Most of the chloride will be reduced to metal. On disappearance of all carbon a drop of nitric acid is added and evaporated, then similarly a drop of hydrochloric acid, and the crucible heated gently, but not to fusion of the silver chloride, and weighed. The chloride is then dissolved in a few drops of warm ammonia water and separated by filtration from the siliceous matter, which latter is ignited and weighed in order to get the weight of the chloride.

This method of procedure is permissible even when the original aqueous extract was quite clear, though the operation then stops with the weighing of the chloride. Or, if very small in quantity, the dry paper with its contents is wound up in a tared platinum wire and carefully ignited after Bunsen's manner. The increased weight of the wire is due to the metallic silver of the chloride which has alloyed with the platinum.

C. DETERMINATION OF ACID-SOLUBLE CHLORINE.

a. BY NITRIC ACID.

If nitric acid will decompose the chlorine-bearing minerals, or if it is desired to distinguish between the chlorine in soluble and in insoluble minerals, the rock powder may be boiled for a few minutes with dilute chlorine-free nitric acid. The acid should be very dilute in order to cause no loss of chlorine, and the boiling should be as brief as possible for the same reason and also to prevent gelatinization of the silica from soluble silicates. Acid as dilute as 1:40 will decompose apatite readily and probably the minerals of the sodalite group, but it is doubtful if anything like this dilution is called for.

The filtrate does not require evaporation for the removal of dissolved silica but may be precipitated at once with silver nitrate. The precipitate is treated as in B, or if at all appreciable in amount may be collected on a Gooch crucible.

b. BY NITRIC AND HYDROFLUORIC ACIDS.

In many cases in order to obtain all the chlorine it is sufficient to attack the powder (which must be much finer usually than the coarse bulk sample) by chlorine-free hydrofluoric and nitric acids in the cold, with occasional stirring, and after filtering through paper fitted into a rubber funnel or large platinum cone to throw down the chlorine by silver nitrate. The presence of nitric acid is necessary, since in its absence ferrous iron in presence of fluorine reduces silver nitrate with deposition of crystallized silver. It may be advisable to redissolve the chloride on the filter in ammonia and to reprecipitate by nitric acid and a drop of silver nitrate. It seems difficult to obtain in the market hydrofluoric acid free from a trace of hydrochloric.

D. DETERMINATION OF CHLORINE BY ALKALI FUSION.

Chiefly because of the difficulty just mentioned, in order to make sure of getting all the chlorine, it is best to fuse with chlorine-free sodium-potassium carbonate, or even sodium carbonate alone, first over the full burner, then for a moment or two over the blast, to leach with water, acidify in the cold with nitric acid, and precipitate by silver nitrate without preliminary separation of silica. After acidification in the cold, except in a very concentrated solution, no precipitation of silica need be feared. The treatment of the precipitate will be as in B or C, according to its amount and freedom from contamination.

25. FLUORINE (SILICA IN PRESENCE OF FLUORINE).

A. GENERAL REMARKS.

There is no direct qualitative test which will reveal with certainty the presence of fluorine in rocks. Heating the powder before the blowpipe with sodium metaphosphate on a curved piece of platinum foil inserted into one end of a narrow glass tube, or in a bulb tube, and noting the presence or absence of etching on the glass where water from the flame condenses, after the tube has been dried, is not to be relied on in all cases. Although in some rocks as little as 0.1 per cent of fluorine can be detected thus with ease, in rocks of another class much larger amounts may fail to show.

The same is true of the direct quantitative methods. Here the result is almost certain to be low and may even be negative when fluorine is present. Those who have given most attention to the subject therefore seem to favor indirect determination, for which only the method given under C, below, is known. Indeed, it is the only one that can be depended upon for fluorine in rocks. However, the preliminary attack of the rock and the subsequent treatment, up to a certain point, are alike for both methods, and as one may be used as a check upon the other both will be described in detail.

For the reason that most of the fluorine minerals occurring in rocks are attacked but partly, if at all, by strong hot sulphuric acid, none of the methods depending on the volatilization of silicon fluoride can be used. There is the further reason that even with decomposable fluorides it is impossible to obtain quantitative results in presence of amorphous silica or silicates.¹ Only with quartz powder or feldspar is volatilization perfect. The method to follow is that of Berzelius, which, though not difficult, requires great attention to details and even then affords low results. (See B. a. γ for causes of error.) It admits of the determination of silica at the same time and is in fact the only method available for silica in fluorides.

B. DIRECT QUANTITATIVE DETERMINATION OF FLUORINE.

a. METHOD OF BERZELIUS.

a. Procedure.—Two grams of the rock powder is fused with four or five parts of sodium-potassium carbonate free from fluorine, avoiding the use of a blast if possible. For minerals rich in fluorine and low in silica it may be necessary to add pure silica before fusing in order to effect complete decomposition of the fluoride, just as with the alkaline-earth phosphates. But probably this will never be required in ordinary rock analysis. To the aqueous extract, containing the fluorine and usually much of the silica besides other bodies, several grams of

¹ See Daniel, K., *Zeitschr. anorg. Chemie*, vol. 38, 1904, pp. 257–306.

ammonium carbonate is added, the liquid is digested at a gentle heat (40°) for some time, and on cooling more carbonate is introduced.¹ After twelve hours the precipitate is collected and washed with water containing ammonium carbonate. From the filtrate the excess of the latter is expelled by evaporating nearly to dryness and the somewhat diluted solution is brought toward neutrality as follows, according to the directions of Treadwell. A few drops of phenolphthalein are added, then nitric acid (not hydrochloric in this case, see below) till the red color disappears. The solution is now boiled, the color reappearing, to be again discharged by acid on cooling. These operations are repeated till it requires but 1 to 1.5 cm.³ of 2 N acid to discharge the color. There is now added 1 to 2 cm.³ of an ammoniacal solution of zinc oxide,² and the liquid is boiled till the ammonia is wholly expelled. The precipitate, containing the last of the silica and some phosphorus, in addition to that thrown down with alumina by ammonium carbonate, is separated and washed with water.

The above-prescribed use of nitric instead of hydrochloric acid for neutralizing is necessitated by the fact that phosphorus, which is almost invariably present, and chromium, must still be removed, and this can be done only from a nitric solution, as follows: To the still alkaline solution silver nitrate is added in excess, whereby phosphate, chromate, chloride if chlorine is present, and carbonate of silver are precipitated. The last serves to correct any acidity resulting from the reaction between the alkaline phosphate and the silver salt, thus producing the neutral solution needed for complete precipitation of the phosphate and chromate. After slight heating and filtering, the excess of silver is removed by sodium chloride and 1 cm.³ of 2 N sodium-carbonate solution is added to the filtrate, which is then boiled in a dish of good size with a large excess of calcium-chloride solution. At this stage there must be no ammoniacal salts in solution, otherwise calcium fluoride may be held up. The precipitate consists of a mix-

¹ The use of ammonium nitrate or chloride, instead of carbonate, for throwing out the silica and alumina is not to be recommended because of loss of fluorine on subsequent evaporation (H. Rose).

² Made by precipitating pure zinc chloride solution with potassium hydroxide, filtering, washing, and dissolving the precipitate in ammonia. Or, more simply, by dissolving zinc oxide in ammonium carbonate solution. If the rocks are very basic, it may happen that the amount of silica in the alkaline solution of the fusion is so small that ammonium carbonate may be dispensed with for its precipitation and the zinc oxide solution added at once, after neutralizing as above.

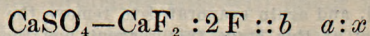
Instead of the ammoniacal zinc oxide solution F. Seemann (*Zeitschr. anal. Chemie*, vol. 44, 1905, p. 343), advocates using the Schaffgotsch solution (p. 213, footnote) in which has been dissolved in the cold 20 grams of freshly precipitated mercuric oxide to the liter. For every 0.2 gram of dissolved silica 100 cm.³ of this reagent is to be used. The solution is then to be evaporated to complete dryness, the residue taken up with water, filtered and washed, the filtrate again neutralized with hydrochloric acid [nitric in rock analysis—W. F. H.], and again evaporated to remove the last of the silica. Where silica is to be determined at this stage this reagent has the advantage over the zinc solution that direct ignition of the precipitates (under a good draft hood) yields at once silica. Its use is manifestly allowable in rock analysis only after the alumina has first been separated by ammonium carbonate.

ture of calcium carbonate and fluoride, the former serving to aid filtration of the latter. The precipitate is collected on paper and washed with hot water, dried, and ignited separately from the filter as far as possible. If the dish used for the precipitation was of platinum, it is not necessary to cleanse it from adhering precipitate, but the contents of the filter are washed back into the dish, the liquid in this is evaporated away, the ash of the filter added, and the dish heated over a free flame to faint redness for a few moments.

Dilute acetic acid is now poured upon the gently ignited mixture in small quantities at a time and in amount slightly in excess of that needed to dissolve the calcium carbonate. When visible action ceases, the liquid is evaporated to dryness and the residue taken up with hot water and a drop of acetic acid, filtered, dried, and ignited gently.

The amount of fluoride obtained from rocks being usually very small, a single treatment as above suffices, but for the larger amounts obtained from fluorine minerals a second and even third treatment with acetic acid may be needed, filtering and igniting after each. S. L. Penfield and J. C. Minor¹ found in such cases that if a great excess of acetic acid is used at the start the results are lower than by the repeated treatment. For considerable amounts, when the loss between two treatments is reduced to not more than half a miligram, F. P. Treadwell and A. A. Koch² take the next to the last weight as correct.

β. *Testing of the calcium fluoride.*—The well-washed and gently ignited calcium fluoride finally obtained in the course of this method should be converted to sulphate as a check on its purity, and at the same time as a qualitative test to ascertain if it really is calcium fluoride by the characteristic odor of the gas given off. Should fluorine be found, and the weight of sulphate not correspond to that of the fluoride, the sulphate should be dissolved in hot nitric acid and tested for phosphorus by ammonium molybdate solution. If phosphate is absent the impurity may have been silica or calcium silicate—which of these it would be difficult to decide. In the former case the fluorine might be safely deduced from the weight of the sulphate, but not in the latter. If the rock were rich in sulphur it might happen that calcium sulphate would be thrown down with the fluoride, but this should be removed by thorough washing. If not, and it were certainly the only impurity present, the fluorine could be calculated, after conversion of the fluoride into sulphate, by the formula



¹ Am. Jour. Sci., 3d ser., vol. 47, 1894, p. 389.

² Zeitschr. anal. Chemie, vol. 43, 1904, p. 469.

in which b is the weight of the sulphate and a that of the impure fluoride.

It is an exceptional case when there is exact agreement between the weight of fluoride and sulphate, and with the small amounts usually met in rocks the error may be an appreciable one in percentage of fluorine, though of no great significance otherwise.

γ. Accuracy of the method.—It is evident from the above that if the greatest care is not taken to prevent any kind of contamination of the weighed fluoride the error in the small amounts in question may be very great. If phosphate were present it would not do to apply the check by conversion to sulphate, because the evaporation with sulphuric acid and following ignition would volatilize metaphosphoric acid.

There is another source of error due to the solubility of the fluoride itself in water and acetic acid. F. P. Treadwell and A. A. Koch¹ have investigated the solvent effect of these and some other reagents. They find that it is possible to detect additional fluorine by repeating the precipitation with calcium chloride in presence of sodium carbonate, and that the total errors are such that for 5 mg. CaF_2 or less the results are much too low, though the qualitative detection still can be made in 100 cm.³ of solution with only 0.0009 gram CaF_2 , notwithstanding the fact that the quantitative tests had seemed to indicate that the loss would be about 0.0015 gram CaF_2 for every 100 cm.³, including wash water. It thus appears that with 1 gram of sample amounts of less than 0.04 to 0.05 per cent of fluorine will escape observation entirely.

A source of error not generally known arises whenever calcium fluoride is ignited in contact with paper. Fluorine escapes to a slight extent and is replaced by oxygen, this reaction being doubtless due to the action of water vapor and not to oxygen of the air.

F. Seeman² subjected all the known methods of determining fluorine to extended examination, using calcium fluoride as his test material, and declares the Berzelius method to be far inferior to those based on volatilization of the fluorine as silicon fluoride, by reason of great and varying losses, the causes of which he was unable to satisfactorily trace. He was unable to recover by it more than about 87 to 89 per cent of the fluorine. My tests, confirmed by other workers, do not support his very unfavorable results. I was able repeatedly to regain 95 to 98 per cent of the fluorine. To do so requires, however, re-fusion of the residue left after leaching the alkali-carbonate melt, including in the same re-fusion the silica precipitated by

¹ Zeitschr. anal. Chemie, vol. 43, 1904, p. 469.

² Idem, vol. 44, 1905, p. 343.

ammonium carbonate and ammoniacal zinc oxide, the treatment of the filtrate from the precipitate of calcium carbonate and calcium fluoride with additional sodium carbonate and calcium chloride, and the reevaporation of the acetic acid solutions of the precipitated calcium carbonate.

D. DETERMINATION OF SILICA IN THE METHOD OF BERZELIUS.

The several precipitates obtained by ammonium carbonate and zinc oxide, together with the residue from the original alkali fusion, are dissolved as far as may be in hydrochloric acid, the papers ignited and their ashes added, and silica is separated by the processes detailed in section 6 (p. 89). These may be greatly simplified, if bases are not likewise to be determined, by evaporating the first filtrate from the silica with much sulphuric acid as in 9. B. a (p. 117) in order to recover the silica which that filtrate always contains. Of course, the determination of silica is not made if it was necessary to add silica when making the original fusion of the rock.

C. OTHER DIRECT METHODS FOR FLUORINE.

Many methods have been devised for the ultimate determination of fluorine in minerals that are decomposed by concentrated sulphuric acid—fluorides and fluophosphates—which it is unnecessary to describe here. All of them depend upon first expelling the fluorine with special precautions, either as silicon fluoride or hydrofluoric acid.

Other methods, devised for fluorides soluble in water, are perhaps applicable to the solution obtained as described in a. α , from which all silicon, aluminum, and phosphorus have been removed, but the same defect that applies to the Berzelius method affects them also, namely, a certain solubility of the precipitate in the precipitating solution. Of these may be mentioned (1) the method of G. Starck,¹ in which the fluorine is thrown down as lead chlorofluoride, $PbClF$; (2) that of F. Pisani,² modified by J. G. Dinwiddie,³ the precipitation being made by calcium sulphate with a resulting mixture of calcium sulphate and fluoride; and (3) that of F. A. Gooch and M. Kobayashi,⁴ the precipitating agent being thorium nitrate.

An excellent digest of the methods for determining fluorine is that given by C. R. Wagner and W. H. Ross.⁵

¹ *Zeitschr. anorg. Chemie*, vol. 70, 1911, p. 173.

² *Compt. Rend.*, vol. 162, 1916, p. 791.

³ *Am. Jour. Sci.*, 4th ser., vol. 42, 1916, p. 464.

⁴ *Idem*, vol. 45, 1918, p. 370.

⁵ *Jour. Ind. Eng. Chemistry*, vol. 9, 1917, p. 1116.

C. INDIRECT QUANTITATIVE DETERMINATION OF FLUORINE.

a. STEIGER'S METHOD.

George Steiger devised in the laboratory of the Geological Survey an indirect method¹ for the determination of fluorine that has met with much favor, although it is not suited for large amounts.

It is based on the well-known fact that the presence of fluorine has a powerful bleaching effect on the yellow color which is produced by the oxidizing of a titanium solution with hydrogen peroxide. A solution of definite volume is made containing the fluorine to be estimated, also having a known amount of titanium present; this is compared in a colorimeter with a second solution containing an equivalent amount of titanium per cubic centimeter, and the bleaching effect recorded. From the extent of this bleaching, the percentage of fluorine can be calculated.

Although the results obtained are not so accurate as those given by many methods for the estimation of other elements, yet considering the difficulty of the fluorine determination, and the time and labor required by methods now in use, the present one may well be employed, where small quantities of fluorine are to be determined. The operations require not only less skill to carry out but are fewer in number and take much less time.

Traces of fluorine amounting to several hundredths of 1 per cent are easily detected, and an approximation to the quantity can be made. In amounts up to a few tenths of a per cent this method seems to be more reliable, and if not more than 2 per cent is present, the results compare favorably in accuracy with the standard methods. It is hardly to be expected, however, to find a colorimetric method using only a few milligrams of the material to be determined that will compare in accuracy with the gravimetric methods using much larger quantities, where considerable percentages of fluorine are concerned.

Sodium salts in large amount make the observed reading for the titanium somewhat low² but not enough to affect the results seriously. Silica in amounts up to 0.1 gram has but little effect, and by the treatment employed its amount is reduced to at most 2 or 3 centigrams. Alumina, which exerts a marked effect, even in small quantities, is readily removed by the preliminary treatment. Phosphoric acid, which bleaches like fluorine, does not interfere unless present in larger amounts than are likely to be encountered in rock analysis.

b. MERWIN'S MODIFICATION OF STEIGER'S METHOD.

α. Introductory remarks.—Merwin, in the paper just cited, not only defined the effect of alkali salts but showed that the concentration of the acid as well as the temperature affects the color of titanium solutions peroxidized by hydrogen peroxide. The salts cause bleaching, while addition of acid counteracts this effect to a considerable degree. Merwin's statements were confirmed by tests made

¹ Jour. Am. Chem. Soc., vol. 30, 1908, p. 219.

² Merwin, H. E., Am. Jour. Sci., 4th ser., vol. 28, 1908, p. 119. Steiger observed a contrary effect, which was probably due to failure to control the acidity of the solution.

at my instigation by William Blum at the Bureau of Standards. Steiger's observations as to the effect of compounds other than alkali salts are in general accord with those of Merwin. Blum further observed that with little acid present the color of the standard and of the bleached test solution can not be matched under certain conditions. This was so, for instance, with 3 milligrams fluorine and 2 per cent sulphuric acid, but with 10 per cent acid a fairly satisfactory comparison was possible with as much as 5 milligrams fluorine.

Merwin gave formulas for computing fluorine in the presence of known amounts of alkali sulphates and acid and modified accordingly the previous methods of getting the fluorine into final solution. He now uses the following procedure, which is taken in part from the paper cited and in part from advance information which he will soon publish.

β. Procedure.—Two grams of rock powder are fused with 8 grams of mixed sodium and potassium carbonates and the fusion is taken up with hot water. When leached, and without the necessity for filtering, there are added 3 or 4 grams of powdered ammonium carbonate. The mixture is warmed for a few minutes and then heated on the water bath till the ammonium carbonate is destroyed and the bulk of the liquid is small. In this way the silica, which otherwise might render the final solution turbid, is thrown down, together with the disturbing alumina and ferric oxide. The destruction of the ammonium carbonate is necessary because ammonium sulphate bleaches the final solution. After filtering there is added to the filtrate—which should not exceed 75 cm.³ in volume—3 or 4 cm.³ of hydrogen peroxide, and then cautiously 10 cm.³ of standard titanium solution¹ (containing 0.01 gram TiO₂). Including the acid in the titanium solution, about 3.5 cm.³ of strong sulphuric acid are required to be added to neutralize the alkali carbonates. As soon as neutrality is reached the solution acquires a light orange color. Neutrality is tested by adding a little sodium carbonate solution to discharge the color, and then a drop or two of acid to restore it. The further treatment depends upon the amount of fluorine expected and the type of colorimeter used. The amount of acid to be added to the neutralized solution depends upon the amount of fluorine present. Therefore, add first 3 cm.³ of concentrated sulphuric acid and make the solution up to 100 cm.³ at a temperature of about 22° and compare at the same temperature with a 100 cm.³ solution containing 0.01 gram TiO₂, 4 cm.³ of H₂O₂ and about 3 cm.³ of concentrated sulphuric acid. The fluorine content of the test solution can then be read off on the curves in figure 22.² If the ratio is greater than about 0.40 the amount of fluorine can be read off accurately. For smaller ratios (more fluorine) more acid should be added to the test solution, a new color comparison made, and a new reading taken from the chart.³ The chart is made on the assumption that the alkali sulphate

¹ The hydrogen peroxide prevents the precipitation of the titanium by the alkali carbonate.

² This chart was prepared recently for me by Dr. Merwin. It was made from new and more accurate data than the former, covering a larger range, but it gives essentially the same fluorine values as the formulas previously mentioned.

³ For certain forms of colorimeter a correction corresponding to the increased volume of the test solution must be made.

corresponds to 8 grams of the half-and-half mixture of potassium and sodium carbonates, or 7 grams of sodium carbonate, used in the fusion. The chart shows, on the zero line of fluorine, the average color ratio for 8 grams of carbonates. The carbonates used for the fusion should be tested in the same way as the filtered solution for the fluorine test. These ratios will probably not differ more than 0.03 from those on the chart. This difference represents about 0.5 milligram of fluorine, which is about the limit of accuracy of the method for amounts of fluorine below 0.006 gram. At about 0.025 gram this limit is about 0.002 gram.

It is very evident that the analyst must take into account the amounts of alkali salts and of acid and must always take his readings at about the same temperature. Anyone who has frequent occasion to determine fluorine in this indirect way should prepare diagrams indicating the corrections to be made under his own conditions of operation.

L. A. Steinkönig¹ has determined the fluorine in a number of soils by a slight modification of the Merwin procedure as given in Bulletin 422. The amounts found were as high as 0.05 per cent.

The method as used "is not delicate enough to indicate with certainty the presence of 0.01 per cent of fluorine," but even so it is a great advance over the gravimetric method for such small quantities.

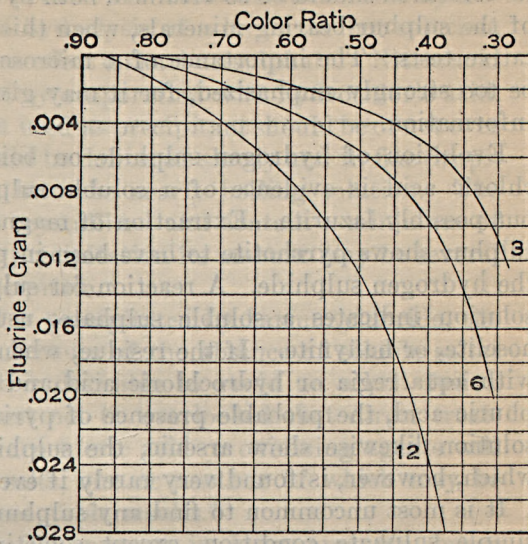


FIGURE 22.—Merwin's diagram for fluorine. Color ratio = $\frac{\text{depth of standard solution}}{\text{depth of test solution}}$. Each solution is peroxidized and made up to 100 cm.³ and contains 0.01 gram of TiO₂. The test solution contains the number of cubic centimeters of concentrated sulphuric acid indicated by the numbers near the curves, and the amounts of fluorine shown, besides sulphates equivalent to 4 grams each of sodium and potassium carbonates. The standard solution contains an indefinite amount of acid between 3 and 5 cm.³. The chart was made at 22°, but it is not significantly different at any temperature between 19° and 25° if both solutions are at the same temperature. If the test solution is 5° warmer than the standard the curves are displaced toward the left hand about 0.02 for 12 cm.³ of acid, and 0.01 for 3 cm.³ of acid. The total color of the solutions is not significantly affected by 10 per cent change of water content.

¹Jour. Ind. Eng. Chemistry, vol. 11, 1919, p. 463.

26. SULPHUR.

A. DETERMINATION OF THE CONDITION OF SULPHUR IN ROCKS.

Before proceeding to the determination of sulphur, when present, its condition should be ascertained, both by microscopic identification of the sulphur-bearing minerals, when this is possible, and by qualitative tests. The importance of a microscopic examination can not be too strongly emphasized, for it may give the analyst most useful information.

Evolution of hydrogen sulphide on boiling with diluted hydrochloric acid is evidence of a soluble sulphide, usually pyrrhotite, but possibly lazurite. Extraction of magnetic particles reacting for sulphur shows pyrrhotite to have been in part at least the source of the hydrogen sulphide. A reaction for sulphuric acid in the filtered solution indicates a soluble sulphate, usually a silicate sulphate, noselite, or haüynite. If the residue, when well washed and treated with aqua regia or hydrochloric acid and bromine, gives more sulphuric acid, the probable presence of pyrite is shown. Should this solution likewise show arsenic, the sulphide may be arsenopyrite, which, however, is found very rarely if ever in igneous rocks.

It is most uncommon to find any sulphur in rocks in the ordinary simple sulphate condition, except sometimes water-soluble traces, even when considerable pyrite is in evidence. The barium of fresh and even moderately decomposed rocks is apparently always in silicates and not in combination with sulphur.

B. QUANTITATIVE METHOD—GENERAL DISCUSSION.

The literature on the determination of sulphur as barium sulphate is very voluminous, and it is only within a comparatively few years that the difficulties attending even an approximately exact determination have become well recognized. Most of the researches made have had to do with the determination of sulphur under conditions where the precipitate of barium sulphate was large, as in the commercially important mineral pyrite. In such cases it is only when the precipitation is made under well-defined conditions that the result is good, and then through compensation of considerable plus and minus errors.

These errors have been attributed to a variety of causes, and various explanations have been offered to account for them. They are referred to in some detail in previous editions of this work. Suffice it to say that they result from occlusion in some manner of chlorine, of alkali metals, and of the ammonium radical and the formation of sulphate compounds that lose sulphur trioxide on ignition. There is no method of treatment that will eliminate en-

tirely all these disturbing factors. In the footnote¹ are listed papers that may be consulted with profit on various phases of the general subject. Particularly useful are those of Allen and Johnston and Johnston and Adams.

In general there should be present the least amount of free hydrochloric acid that will prevent hydrolysis of salts in the hot solution, for the acid has marked solvent effect on barium sulphate. Nitric acid should be avoided or removed by evaporation with hydrochloric acid. The barium chloride solution used as precipitant should be of not over 10 per cent strength and should be delivered slowly and in fine drops, if much sulphur is present, into the nearly boiling solution. The precipitate then will be well crystallized and contain a minimum of chlorine, whereas with rapid precipitation its amount may be several milligrams per gram of precipitate.

When pure sulphuric acid is precipitated by barium chloride, the problem is relatively simple because of the absence of soluble salts; hence in mineral analysis it is desirable to avoid an alkali fusion whenever possible, but it must not be overlooked that direct treatment of the mineral with hydrochloric acid or oxidizing agents will extract certain amounts of salts, one or another of which may be fatal to the attainment of acceptable results.²

In rocks sulphur is not often present in large amounts, hence special precautions in making the precipitation or special purification of the barium sulphate are hardly ever necessary, especially as the precipitation is usually made in the absence of iron.

C. QUANTITATIVE DETERMINATION IN ROCKS.

a. TOTAL SULPHUR.

Although sometimes the sulphur of sulphides may be extracted wholly with aqua regia or some other powerful oxidizer, in the

¹ Hulett, G. A., and Duschak, L. H., *Zeitschr. anorg. Chemie*, vol. 40, 1904, p. 196. Lunge, G., and Stierlin, R., *Zeitschr. angew. Chemie*, vol. 18, 1905, p. 1921. Lunge, G., *Rept. Eighth Internat. Cong. Appl. Chemistry*, Rome, 1906, p. 399. Hintz, C., and Weber, H., *Zeitschr. anal. Chemie*, vol. 45, 1906, p. 31. Föllin, O., *Jour. Biol. Chemistry*, vol. 1, 1906, p. 131. Van't Kruys, M. J., *Chem. Weekblad*, vol. 6, 1909, p. 735; *Zeitschr. anal. Chemie*, vol. 49, 1910, p. 393. Allen, E. T., and Johnston, J., *Jour. Am. Chem. Soc.*, vol. 32, 1910, p. 588. Allen, E. T., and Johnston, J., *Jour. Ind. Eng. Chemistry*, vol. 2, 1910, p. 196; *Chem. News*, vol. 101, 1910, pp. 257, 267; *Zeitschr. anorg. Chemie*, vol. 69, 1910, p. 102. Johnston, J., and Adams, L. H., *Jour. Am. Chem. Soc.*, vol. 33, 1911, p. 829; *Chem. News*, vol. 105, 1912, pp. 162, 173, 183. Huybrechts, M., *Bull. Soc. chim. Belgique*, vol. 24, 1911, p. 177. Smoot, A. M., *Eng. and Min. Jour.*, vol. 94, 1913, p. 412. Smith, G. McP., *Jour. Am. Chem. Soc.*, vol. 39, 1917, p. 1152. Winkler, L. W., *Zeitschr. angew. Chemie*, vol. 30, 1917, pp. 251, 259, 281. Karaoglanow, Z., *Zeitschr. anal. Chemie*, vol. 56, 1917, pp. 225, 417, 561; vol. 57, 1918, pp. 77, 113.

² Smoot (op. cit.) in analyzing pyrite eliminates iron and other heavy metals by electrolysis, using a mercury cathode for collecting the metals. The solution then carries practically only free sulphuric acid, from which the sulphate radical can be precipitated with less error than when iron, alkali, or ammonium salts are present. The device has been used under other conditions to separate elements that do not lend themselves to effective separation when together.

wet way, this is not always so. Therefore it is generally better by far to fuse with sulphur-free sodium carbonate and a little niter over the Bunsen burner, and for a few moments over the blast, using throughout the heating the arrangement shown in figure 3 (p. 34), in order to exclude access of sulphur from the flame gases. This determination may be combined very conveniently with that of barium, titanium, zirconium, and rare earths (p. 170). After thorough disintegration of the fusion in water, to which a drop or two of alcohol has been added for the purpose of reducing and precipitating any manganese dissolved as manganate, the solution is filtered and the residue washed with a dilute solution of sodium carbonate. In the filtrate (100 to 250 cm.³ in bulk) the sulphur is precipitated at boiling heat or on the steam bath by barium chloride in excess, after slightly acidifying in the cold by hydrochloric acid. Evaporation to dryness first with acid, in order to eliminate silica, is needless, for in the above bulk of solution there will almost never be the least separation of silica with the barium sulphate.¹ It is well that this is so, for evaporation on a bath heated by gas, in order to remove silica, would involve in many cases an error fully equal to the sulphur present, by contamination from the sulphur of the gas burned. With a steam bath this difficulty does not present itself. Should there be fear of a trace of silica being present, it can be removed by a drop of hydrofluoric and sulphuric acids before weighing the barium sulphate.

In order to reduce greatly the error caused by the presence of sodium chloride resulting from the sodium carbonate used in the fusion, W. A. Turner² reduces the solution to a small volume (25 cm.³), saturates it with hydrochloric acid gas, or adds concentrated hydrochloric acid (five times the volume of the solution concentrated to 10 cm.³), filters through a Gooch crucible, washes with strong hydrochloric acid, evaporates the filtrate, filters again if need be, and precipitates with barium chloride. This seems to be an excellent suggestion.

Errors due to the solvent action on the barium sulphate of hydrochloric acid or of ammonium or fixed salts in the solution can usually be corrected by evaporating the filtrate from the barium sulphate, destroying or expelling ammonium salts if present, treating the residue with water slightly acidified with hydrochloric acid, and

¹ The results of C. W. Stoddart (*Jour. Am. Chem. Soc.*, vol. 24, 1902, p. 852) show, in the determination of sulphur in coals by the Eschka method, often higher sulphur when silica is not removed by evaporation in the usual way, but this is contrary to all my experience in silicate work, where duplicates agree usually exactly, and if they differ are as likely to be high by one way as by the other. The explanation may be that Stoddart acidified his solutions hot or used too strong an acid and had some silica precipitated.

² *Am. Jour. Sci.*, 4th ser., vol. 38, 1914, p. 41; *Zeitschr. anorg. Chemie*, vol. 88, 1914, p. 412; *Chem. News*, vol. 111, 1915, p. 100.

collecting and purifying the barium sulphate that may be left undissolved.

B. FRACTIONAL DETERMINATION.

When sulphur is present in more than one condition it is usually desirable to know the respective amounts, hence fractional determinations must be made.

If traces of sulphates soluble in water are present, they can be removed by extraction with boiling water.

For the quantitative extraction of the sulphur of all soluble sulphates, simple boiling with hydrochloric acid suffices, which should be done in an atmosphere of carbonic acid if pyrites or other oxidizable sulphides are present, and should be finished as quickly as possible in order to minimize the error resulting from oxidation to sulphuric acid of the sulphur of sulphides, if present, by any ferric salts that may have been dissolved.

If soluble sulphates and sulphides as well as insoluble sulphates and sulphides are present together, the sulphur of the first is found in solution after extraction by hydrochloric acid in a carbon-dioxide atmosphere, and that of the decomposable sulphides by collecting the hydrogen sulphide evolved.¹ Then in the residue the sulphur of the insoluble sulphides can be determined after suitable oxidation, and in the resulting residue that of the insoluble sulphates after fusing with sodium carbonate. The sulphur of the insoluble sulphates can, however, be calculated by subtracting the barium sulphate equivalent of the preceding fractional determinations from that found for the total sulphur.

The error involved in the above estimation of the sulphur of soluble sulphides, due to the possible reducing effect of hydrogen sulphide on ferric salts, is probably negligible. Most of the hydrogen sulphide would be expelled before any such action could take place and probably before the ferric salts were largely attacked, but of course the small proportion of sulphur set free as such from pyrrhotite would escape estimation and introduce further uncertainty. In general, it would be safe enough to assume the composition Fe_7S_8 for pyrrhotite.

Obviously, such a procedure as that given above is open to many errors, especially with the more complex mixtures, and however carefully all these separate determinations may be carried out, the final figures for ferrous and ferric oxides can hardly be regarded as more than approximations when much sulphide is present. (See 21, D. c. α , p. 201).

¹ With pyrrhotite a small fraction of its sulphur—one-eighth if the formula Fe_7S_8 is adopted—is liberated as free sulphur and not as hydrogen sulphide.

27. BORON.

A. GENERAL REMARKS.

No doubt boron occurs occasionally in rocks in amounts superior to those of some of the other constituents that are habitually determined. But the lack of precision of the methods that are at all applicable to mineral substances not directly soluble in acids other than hydrofluoric acid is accountable for the fact that no one has ever sought to apply these methods to rocks, unless boron was supposed to be present in appreciable amount. When this condition is fulfilled it is customary to fuse with an alkali carbonate and then apply in one of its numerous modifications the Rosenbladt-Gooch method. In the footnote below¹ are given the most important references that relate to the development of this method and its application to refractory minerals.

The method depends on expelling the boron as methyl ester by distillation with methyl alcohol from an acid solution, collecting the ester in some suitable manner and then determining the boron gravimetrically or volumetrically. For simple borates, especially the soluble ones, the method gives satisfaction when all needful precautions are carefully observed, and that it may do so also with refractory borosilicates has been shown by several workers, most

¹ Th. Rosenbladt (*Zeitschr. anal. Chemie*, vol. 26, 1887, p. 21) used magnesia for binding the boron, while F. A. Gooch (*Proc. Am. Acad. Arts and Sci.*, 1886, p. 167; *Bull. U. S. Geol. Survey* No. 42, 1887, p. 64; *Chem. News*, vol. 55, 1887, p. 7) preferred lime as more active and reliable. Gooch and L. C. Jones have later (*Am. Jour. Sci.*, 4th ser., vol. 7, 1899, p. 34; *Chem. News*, vol. 79, 1899, pp. 99, 111) upheld the use of lime and proposed as a convenient though perhaps not quite so perfect substitute, sodium tungstate containing an excess of tungstic oxide. In this article they likewise indicate the precautions now used to insure complete collection and retention of the boron.

For a useful modification in the way of collecting the boric ether in ammonia before bringing in contact with the lime, see S. L. Penfield and E. S. Sperry (*Am. Jour. Sci.*, 3d ser., vol. 34, 1887, p. 222); also H. Moissan (*Compt. Rend.*, vol. 116, 1893, p. 1087; *Bull. Soc. chim.*, vol. 12, 1894, p. 955), who modifies the Gooch distilling apparatus in certain respects.

G. W. Sargent (*Jour. Am. Chem. Soc.*, vol. 21, 1899, p. 858) obtained satisfactory results with tourmaline by collecting the boron in sodium-hydroxide solution, neutralizing the alkali with hydrochloric acid by the aid of methyl orange, then titrating the freed boric acid by sodium hydroxide in presence of glycerin, using phenolphthalein as indicator (method of Thompson, *Jour. Soc. Chem. Ind.*, vol. 12, 1893, p. 432).

Later contributions to the application of this method are by R. J. Manning and W. R. Lang (*Jour. Soc. Chem. Ind.*, vol. 25, 1906, p. 396), who determine the boron in the distillate gravimetrically as the barium salt $Ba(BO_2)_2$, and by Wilson H. Low (*Jour. Am. Chem. Soc.*, vol. 28, 1906, p. 807), who modifies the distillation feature, with much apparent advantage, by the addition of dry granulated calcium chloride and perfects the turmeric-paper qualitative test. This author titrates the distillate in presence of glycerin. W. H. Chapin (*Jour. Am. Chem. Soc.*, vol. 30, 1908, p. 1691) applies the Low method successfully with slight modifications to borosilicates but prefers mannite to glycerin. E. T. Wherry (*Jour. Am. Chem. Soc.*, vol. 30, 1908, p. 1687) devised a method for refractory boron minerals that yielded him results comparing favorably with those of Chapin, the same samples being used. It depends on separating aluminum and iron by means of calcium carbonate in a special manner, after making an alkali fusion, and titrating the filtrate directly in presence of mannite. The aluminum and iron must, however, be redissolved and reprecipitated one or more times.

recently by Chapin. Before Chapin's work it was considered necessary to extract with water the alkaline fusion of a mineral and to treat the extract for the boron. The wide divergence of results obtained by different chemists, even between duplicate results by the same analyst, is probably referable to the employment of only a single fusion and extraction, for it has been shown by S. L. Penfield and H. W. Foote,¹ by G. W. Sargent,² and by W. E. Ford³ that these operations must be repeated. A decided advance seems to have been scored by Chapin, who shows that aluminum and iron need not be removed but that the carbonate melt may be dissolved directly in acid without prejudice to the accuracy of the method as carried out by him. Furthermore, the presence of chlorine, even of fluorine, does not seem to be detrimental. Possibly his procedure may yet prove applicable to rocks as well as to boron minerals.

Mainly in the hope of stimulating search for boron in rocks the Chapin procedure is given in detail below.

B. DISTILLATION METHOD AS MODIFIED BY CHAPIN.

a. REAGENTS.

1. *Paranitrophenol*.—One gram dissolved in 75 cm.³ of neutral ethyl alcohol and made up to 100 cm.³ with water.

2. *Phenolphthalein*.—One gram dissolved in 100 cm.³ of ethyl alcohol and made up to 200 cm.³ with water.

3. *Hydrochloric acid, 0.1 normal*.—The water should be boiled to remove carbonic acid.

4. *Hydrochloric acid, 1.1 strength*.—A dropping bulb should be filled with this acid when it is needed in accurate small amounts.

5. *Sodium hydroxide, 0.5 and 0.1 normal*.—These should be standardized as follows: Fuse pure boric acid in a platinum dish. While still warm break the melt up and place the fragments quickly in a weighing tube. Dissolve 1.75 grams in 250 cm.³ of hot, recently boiled water, cool, and dilute the solution to 500 cm.³ This solution is 0.1 normal—that is, in presence of mannite or glycerol 1 cm.³ is neutralized to the phenolphthalein end point by 1 cm.³ of 0.1 normal sodium hydroxide.

In standardizing the sodium hydroxide against this solution both indicators should be used, so that the end may be the same as that seen in actual titration. Follow exactly the directions given under b, below, for the final titration, only assuming that the boric acid solution is exactly neutral to paranitrophenol—that is, free from

¹ Am. Jour. Sci. 4th ser., vol. 7, 1899, p. 97.

² Jour. Am. Chem. Soc., vol. 21, 1899, p. 858.

³ Am. Jour. Sci., 4th ser., vol. 14, 1903, p. 195.

mineral acid. When sodium hydroxide is standardized in this way the small amount of carbonate present does no harm.

6. *Mannite*.—This is preferable to glycerol, for it requires no special preparation, does not materially increase the bulk of the solution to be titrated, and gives an equally sharp end point.

7. *Methyl alcohol*.—This should be distilled over lime after it has been heated for some hours in contact with the lime under a reflux condenser. The more nearly anhydrous the alcohol is the better.

8. *Calcium chloride*.—This should be granular, anhydrous, and free from boron.

b. APPARATUS.

The main set up of the apparatus required is shown in figure 23.

c. PROCEDURE.

Chapin used not more than half a gram of mineral powder for even very small amounts of boron, and not less unless the percentage exceeded 10. When the percentage is high it is best to so limit the weight of the sample that the amount of B_2O_3 shall not exceed 0.1 gram. If a flux is used it should be weighed to within a milligram or two; then the amount of acid required to take up the melt can be measured out at once and there is no danger of using too great an excess.

If the mineral is soluble in hydrochloric acid, transfer 1 gram of it to the flask B, without letting any adhere to the neck, and treat with not more than 5 cm.³ of 1:1 hydrochloric acid. Heat gently on a water bath until solution is complete.

If the mineral is not soluble, add to it exactly six times its weight of sodium carbonate or of an equimolecular mixture of sodium and potassium carbonates, mix, and fuse in the usual manner. Without removing from the crucible, decompose the melt with 1:1 hydrochloric acid in calculated amount added by degrees. While this is being done the crucible should rest in a casserole, and the lid should be kept in place as much as possible. Toward the end it may be necessary to heat a little, but care should be taken not to boil, for boric acid would be lost with the steam. Pour the solution into the flask B and rinse the crucible with a very little water.

Then add pure anhydrous calcium chloride, using about 1 gram for each cubic centimeter of solution and running it through a paper funnel to keep the neck of the flask clean. Twirl the flask a little to allow the chloride to take up the water, connect it with the rest of the apparatus, raise the casserole beneath it until the flask rests in the water but does not touch the bottom, and then begin the distillation of the alcohol from flask A, taking care that the open end

of the capillary "boiling tube" is free from alcohol and that the U tube attached to the receiver is trapped with water.

The decomposition flask, B, is not heated until about 25 cm.³ of alcohol has condensed in it. After that the water bath is heated by

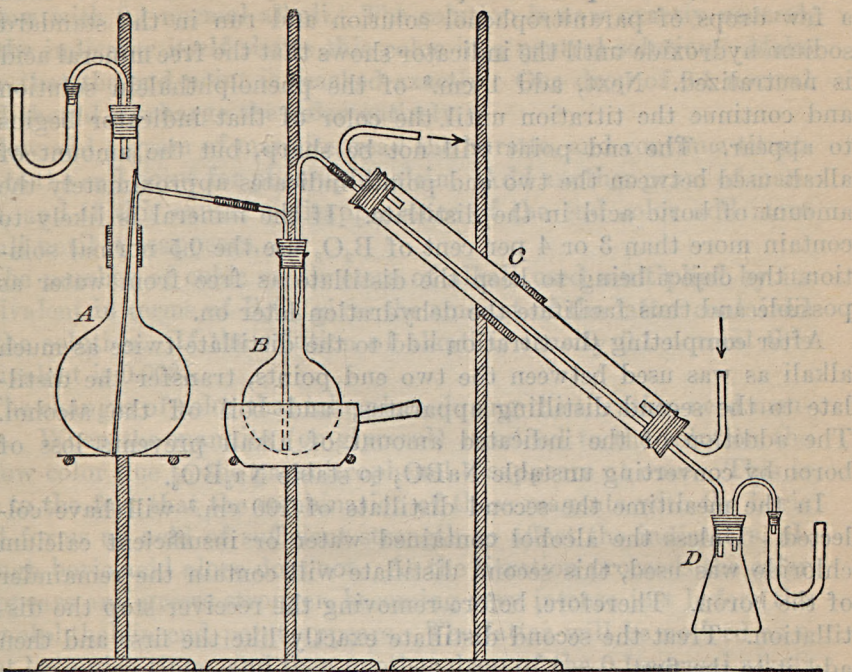


FIGURE 23.—Distilling apparatus for boron.

- A. Flask of 500 cm.³ capacity for methyl alcohol, having a U tube containing a little mercury as a safety trap, and a capillary "boiling tube" 3 mm. in bore, the bore closed at 1 cm. from the lower end.
- B. Flask of 250 cm.³ capacity, supported in a casserole of water but not touching the bottom. The outlet tube of B should be not less than 12 cm. in vertical height and of rather wide bore. The end inside the flask should be jagged to allow condensed liquid to drop back instead of jumping up the tube.
- C. Glass condenser, 40 cm. long, of tubing 3 cm. wide.
- D. Receiving flask of 250 cm.³ capacity. Two or three of these flasks should be at hand, with necks of the same size, so that the receiver can be changed without interrupting the distillation. The small U tube attached contains a little water to prevent the escape of any uncondensed methyl borate.
- E. (Not shown.) A second glass condenser like C, connected on the one side to a flask exactly like B, which, however, has a stopper with only one hole and rests completely within a large bath. The flask carries also a "boiling tube." On the other side is a receiver like D, but without the U trap. This apparatus is used for distilling off the alcohol after the preliminary titration.
- F. (Not shown.) Filter pump. At the end of the side tube is an elbow tube connected to a rubber stopper with two holes and of a size to fit the flask mentioned in connection with E. The second hole of the stopper is closed by a glass plug, which can be withdrawn to break the vacuum. Midway between pump and stopper is a small safety bottle, to prevent the tap water from sucking back into the flask.

a small flame and the flask thus kept hot enough to prevent further condensation of alcohol. The distillation should not be so rapid as to permit escape of methyl borate from the system.

When a distillate of about 100 cm.³ has collected the receiver is exchanged for a fresh one and the collection of a second distillate is proceeded with. The contents of the trap tube are added to the first receiver, and a preliminary titration is made as follows: Add a few drops of paranitrophenol solution and run in the standard sodium hydroxide until the indicator shows that the free mineral acid is neutralized. Next, add 1 cm.³ of the phenolphthalein solution and continue the titration until the color of that indicator begins to appear. The end point will not be sharp, but the amount of alkali used between the two end points indicates approximately the amount of boric acid in the distillate. If the mineral is likely to contain more than 3 or 4 per cent of B_2O_3 use the 0.5 normal solution, the object being to keep the distillate as free from water as possible and thus facilitate the dehydration later on.

After completing the titration add to the distillate twice as much alkali as was used between the two end points, transfer the distillate to the second distilling apparatus, and boil off the alcohol. The addition of the indicated amount of alkali prevents loss of boron by converting unstable $NaBO_2$ to stable Na_3BO_3 .

In the meantime the second distillate of 100 cm.³ will have collected. Unless the alcohol contained water or insufficient calcium chloride was used, this second distillate will contain the remainder of the boron. Therefore, before removing the receiver stop the distillation. Treat the second distillate exactly like the first and then add it to the first.

If the amount of alkali used for titrating the second distillate is less than 0.1 cm.³ of the 0.1 normal solution the distillation may be regarded as complete.

When the liquid from which the alcohol is being distilled no longer boils in the steam bath, remove it to a casserole, rinsing the flask once or twice with water, and heat over a direct flame, rotating the casserole while doing so, until the little remaining alcohol has been boiled out. The residue should now be small—about 25 cm.³ if 0.1 normal alkali was used and much less if 0.5. If the volume is less than 25 cm.³ make up to that extent.

Return the solution to the flask and add drop by drop with constant twirling 1:1 hydrochloric acid from a dropping bulb, until the color of both indicators is discharged, taking care not to add a drop too much. Now put in the "boiling tube," heat the flask in the steam bath for a minute or two, then attach to the filter pump and boil under reduced pressure until the liquid is nearly cold and only an occasional bubble appears. All carbon dioxide being thus removed, break the vacuum, cool if necessary under the tap, and proceed to the final titration.

First neutralize the excess of hydrochloric acid by running in carefully 0.5 normal sodium hydroxide until the yellow of paranitrophenol just appears. Bring back to acid reaction with 0.1 normal hydrochloric acid and then to the appearance of a faint yellow with 0.1 normal alkali. The solution is now exactly neutral, as the indicator itself shows this color in a neutral solution. Make sure that the end point is reached exactly. One drop of 0.1 normal acid should discharge the color entirely.

Now add 1 gram of mannite, read the burette, and continue titrating to the end point for phenolphthalein. Add another gram of mannite, and if this causes a disappearance of the end color add more alkali until it reappears.

The number of cubic centimeters of alkali used multiplied by its equivalent in terms of B_2O_3 gives the amount of the latter contained in the solution. If the solution of alkali is exactly 0.1 normal this equivalent is 0.0035.

The changes of color that take place during the titration need mention. When the mannite (or glycerol) is added to the solution the yellow color due to the paranitrophenol disappears at once. This is due to the fact that the combination of these reagents with the boric acid forms an acid of sufficient strength to affect the indicators, although boric acid alone does not. As the titration proceeds the color reappears and grows stronger, becoming very intense just before the phenolphthalein end point appears. The latter will be noticed as a faint brownish tinge, and then another drop of the 0.1 normal alkali changes it to an intense brownish red, which is the real end point.

Compared with the time required for gravimetric determinations that necessary to carry out this method is not excessive. After apparatus and reagents are ready a series of four determinations may be run easily in eight hours.

E. T. Allen and E. G. Zies¹ tested the Chapin method very fully in its application to the determination of boron in glasses and regard it as far superior to other methods, even though it is subject to a slight but very uniform correction of 1 milligram or less, to be determined by a blank run. The correction seems to be due always in part to a boron content of the reagents used and in part to a titration error. The fact that such correction is unavoidable makes the method of uncertain value for determining the very small amounts of boron that rocks may be presumed to carry, but the constancy of results is so great that a consistent excess found over what the blank affords is strong evidence that boron is actually present.

Allen and Zies found the method to be affected appreciably by relatively large amounts of arsenious acid but not by arsenic acid. The

¹ Jour. Am. Ceramic Soc., vol. 1, 1918, p. 739.

effect of the former can be eliminated by converting it to arsenic acid by oxidizing with hydrogen peroxide after making the solution distinctly alkaline with sodium hydroxide.

Allen and Zies also found that relatively large amounts of fluorides affect the accuracy of the method but do not seriously impair its usefulness for ordinary work.

C. QUALITATIVE TESTS FOR BORON.

The detection of very small amounts of boron in rocks is not a simple test. E. T. Wherry and W. H. Chapin¹ found the limit of sensibility of the direct flame test to be 0.2 per cent. The test is made by mixing the mineral powder with potassium bisulphate and calcium fluoride and introducing it on a clean platinum wire into the nonluminous Bunsen burner flame. A green color imparted to the flame, appearing only as evanescent flashes toward the lower limit of sensitiveness, is indicative of boron if no other elements are present that might give a green color.

Applied to distillates as obtained under B, above, the color imparted to the flame of burning alcohol by its boric ester affords a much more delicate test, as shown by C. Mannich and H. Priess,² V. Lenher and J. S. C. Wells,³ and others.

The turmeric paper test as carried out by W. H. Low⁴ gave Wherry and Chapin a distinct positive test for boron in a mineral carrying 0.08 per cent B_2O_3 . Low's procedure is as follows: In the boric solution acidified with hydrochloric acid and contained in a shallow dish (not glass of the boro-silicate type) is placed a piece of turmeric paper. The solution is then evaporated to complete dryness in a desiccator. Boron imparts a pinkish-red color to the paper if no interfering element, such as titanium, or too much hydrochloric acid, is present. The test is not applicable directly to the solution of a mineral, but only to distillates obtained as described under B, above.

The turmeric test is the most delicate of all when made with the precautions taken by G. Bertrand and H. Agulhon,⁵ for which reference must be made to the original publications. These authors applied the tests for amounts of boric oxide ranging from 0.1 milligram down to 0.0005 milligram. Specially prepared reagents must be used. E. T. Allen and E. G. Zies⁶ have used the method with success. The basis of the test is the length of coloration imparted to small strips

¹ Jour. Am. Chem. Soc., vol. 30, 1908, p. 1684.

² Chem. Zeitung, vol. 32, 1908, p. 314.

³ Jour. Am. Chem. Soc., vol. 21, 1899, p. 417.

⁴ Idem, vol. 28, 1906, p. 807.

⁵ Compt. Rend., vol. 157, 1913, p. 1433; Bull. Soc. chim., vol. 7, 1910, pp. 90, 125; vol. 13, 1913, p. 396.

⁶ Op. cit.

of turmeric paper dipping into like volumes of the test solution and of several standard solutions contained in small graduates. The solutions drawn up by capillarity evaporate at the exposed ends of the strips, and after some hours these appear colored for different lengths according to the amounts of boron present in the different solutions. With a sufficient number of standard solutions the test yields fairly accurate quantitative results. Application of ammonia turns the color blue.

28. CERTAIN CONSTITUENTS IN MINUTE TRACES.

If, as sometimes may happen, the problem is presented of examining rocks for traces of gold, silver, and other elements which are not ordinarily looked for, as in F. Sandberger's investigations bearing on the origin of the metalliferous contents of veins, large weights of material must be taken, up to 50 grams or more. This involves the use, also, of large quantities of reagents, the purity of which must be looked to with the utmost care. Special directions to meet such cases can not then be given here, nor even a complete reference list of the scanty and scattered literature on this subject. Sandberger's own writings deal but little with its analytical side, and from its inaccessibility in the Washington libraries I am as yet unacquainted with the report by H. von Foullon,¹ "Ueber den Gang und die Ausführung der chemischen Untersuchung," following Sandberger's own paper² in the general report "Untersuchungen der Nebengesteine der Pribramer Gänge." I have published a few data as to gold, silver, lead, zinc, etc.,³ in S. F. Emmons's report on "The geology and mining industry of Leadville;" J. S. Curtis,⁴ in his report on "The silver-lead deposits of Eureka, Nev.," has given his method of assaying rocks for traces of gold and silver; in volume 7 of the Reports of the Missouri Geological Survey, page 740, are to be found the methods used by James D. Robertson for the determination of lead, zinc, and copper in silicate and carbonate rocks of Missouri. The earlier work of J. G. Forchhammer⁵ and L. Dieulaufait,⁶ the latter of whom examined many hundreds of Archean rocks,

¹ Jahrb. der Bergakad. Leoben u. Pribram, 1887, p. 363.

² From Sandberger's report it appears that the rocks were treated successively with water, acetic acid, boiling dilute hydrochloric acid for two days, and finally hydrofluoric acid, the several extracts and final residue of fluorides (and pyrite) being separately examined for heavy metals. The products of distillation were also examined. A striking fact observed in all cases was the complete insolubility of the pyrite, even after the severe treatment mentioned. This speaks strongly in favor of the correctness of ferrous iron estimations in silicates by the hydrofluoric and sulphuric acid method when pyrite is present unaccompanied by other sulphides. (See 21. D. c. 4, p. 201.)

³ Mon. U. S. Geol. Survey, vol. 12, 1886, Appendix B, pp. 592-596.

⁴ Idem, vol. 7, 1884, pp. 120-138.

⁵ Poggendorff's Annalen, vol. 95, 1855, p. 60.

⁶ Annales chim. phys., vols. 15, 17, 18, 21, 1878-1880.

was of a qualitative nature. More recent papers on the dissemination and determination of traces of gold are those of J. R. Don¹ and L. Wagoner.²

29. THE GASES AND VAPORS EXPELLED BY HEAT.

That rocks and minerals evolve large quantities of gases and vapors when heated is a well-recognized fact. Numerous analyses have shown, that the volatile products usually comprise hydrogen and carbon dioxide as preponderating constituents, with carbon monoxide, methane, nitrogen, hydrogen sulphide, etc., in smaller amounts. The total volume may be many times that of the solid. To a certain extent, sometimes a large extent, especially as to carbon dioxide, the source of these is entrapped fluid inclusions, whose origin was contemporaneous with that of the containing minerals. A further portion may have been held dissolved in the rocks, particularly in those not wholly crystallized. But from the experiments of some recent investigators, especially Morris W. Travers,³ A. Gautier,⁴ K. Hüttner,⁵ and R. T. Chamberlin,⁶ it is very evident that the gases are often produced by chemical changes resulting from the heat used for their expulsion. Thus, hydrogen may be due to reduction of water by minerals susceptible of oxidation at high temperatures, as ferrous silicates; the carbon monoxide to reduction of carbon dioxide in a like manner or by the hydrogen formed by the first reaction; the methane might arise from interaction between water and traces of metallic carbides, etc.⁷

Free oxygen is not reported as one of the evolved gases, and from the nature of the case it should hardly be expected.

Nitrogen, though found in but small relative amount in the free state, is comparatively abundant and easily detectable as ammonia or ammonium salts in certain classes of rocks and long since was thus recognized. H. Rose⁸ says that pitchstone gives off ammoniacal water on heating; A. Delesse⁹ found ammonia in rocks, and A. Gautier later made quantitative tests; H. Erdmann¹⁰ found that ammonia was

¹ Trans. Am. Inst. Min. Eng., vol. 27, 1897, p. 564.

² Idem, vol. 31, 1901, p. 808.

³ Proc. Roy. Soc., vol. 64, 1899, p. 130.

⁴ Compt. Rend., vol. 131, 1900, p. 647; vol. 132, 1901, pp. 58, 189; vol. 136, 1903, p. 16; Annales chim. phys., 7th ser., vol. 22, 1901, p. 97; Annales des mines, 10th ser., vol. 9, 1906, p. 316.

⁵ Zeitschr. anorg. Chemie, vol. 43, 1905, p. 8.

⁶ The gases in rocks, Carnegie Inst. Washington, 1908. This is a very complete discussion of the subject, supplemented by a mass of experimental data.

⁷ For the methods of collecting and analyzing such gaseous mixtures consult Travers, M. W., The experimental study of gases; the above-cited papers of Gautier; and Moureu, Charles, Compt. Rend., vol. 142, 1906, p. 44.

⁸ Quantitative Analyse, Finkener ed., p. 673.

⁹ Annales des mines, vol. 18, 1860, p. 151.

¹⁰ Ber. Deutsch. chem. Gesell., vol. 29, 1896, p. 1710.

obtained by acting on various minerals of ancient igneous rocks with a caustic alkali; C. Luedeking and H. A. Wheeler¹ found ammonium sulphate in a barite from Missouri, the presence of which I was able to confirm.

It has been noted in this laboratory on three separate occasions when series of ores, roofing slates, and eruptive rocks were analyzed, that ammonia, either in the form of chloride or sulphate, or even as free ammonia, was given off on heating. Its appearance was not limited to one or a few specimens of a series but seemed to be characteristic of all and to be afforded by the unbroken rock as well as by the powdered sample. The precise conditions under which the specimens were collected not being known, it is impossible to affirm positively that the ammonia may not have been due to recent organic contamination of some sort, especially in the case of the slates, but it is believed that a more critical collection of material will not alter the general result. Its amount was sometimes readily determinable by Nesslerization, being as high as 0.04 per cent in some slates. Carbonaceous organic matter was absent from most of these, but doubtless existed in them in their early history. In their case the ammonia was evolved as such, in part, at least, and imparted a strong alkaline reaction to the water in the upper part of the tube. The presence of sulphides, fluorides, or chlorides in the rock might cause the ammonia to appear as a sublimate of sulphate, fluoride, or chloride. It has been suggested that ammonia might result from the action of water on metallic nitrides, O. Silvestri² having observed a nitride of iron on a lava from Etna.

30. SPECIAL OPERATIONS.

The problem presents itself often of ascertaining the composition of that portion of a rock powder which is soluble in special reagents or in a reagent of a particular concentration. No precise directions can be formulated to meet such cases. The procedure must vary with the character of the constituents of the rock and with the object which it is sought to attain, and only in exceptional cases can a separation of this kind be sharp. Much depends on the degree of fineness of the powder and on the length of time it is exposed to the action of the reagent.

A. DETECTION OF NEPHELINE IN PRESENCE OF OLIVINE.

For confirmation of the microscopic diagnosis, L. V. Pirsson³ has indicated a means of detecting nepheline in presence of olivine, as in nepheline basalts, based on the very ready solubility of nepheline,

¹ Am. Jour. Sci., 3d ser., vol. 42, 1891, p. 495.

² Gazz. chim. ital., vol. 5, 1875, p. 301.

³ Am. Jour. Sci., 4th ser., vol. 2, 1896, p. 142.

as compared with olivine, when boiled for but one minute with a sufficiency of very dilute nitric acid (1:40). Gelatinization of the filtrate on evaporation is taken as evidence of the presence of nepheline. If olivine is present in quantity, however, this test must not be accepted at once as final, for some if not all olivines are much more soluble in nitric acid of the above strength than Pirsson was led to believe from his original tests. If, therefore, on evaporation of the filtrate, much iron is indicated, the gelatinization may be due to olivine alone or in part, and then the quantitative relation of silica to iron plus magnesium should be ascertained. It must be borne in mind also that any other very soluble silicates present will be more or less affected, and that apatite is largely or wholly dissolved. It is possible that still more dilute nitric or perhaps some other acid may exert a slighter solvent action on olivine without being appreciably less effective in dissolving nepheline, etc. In combination with a quantitative analysis of the extract the method is perhaps susceptible of a wider application than the particular case for which it was first used. It is well worth further study.

B. DETERMINATION OF "SOLUBLE" SILICA.

Very often in treatment by acids silica is separated in gelatinous or granular form mixed with the unattacked minerals, and it becomes necessary to remove or estimate this silica, or else to discriminate between soluble and insoluble silica already existing together. Usually a boiling solution of sodium carbonate has been employed for this purpose, though the caustic alkalies have found advocates.

G. Lunge and C. Millberg¹ have shown conclusively that quartz is not nearly so insoluble in solutions of the caustic alkalies as has been supposed, but that given a sufficient degree of subdivision it can be brought wholly into solution; that it is impossible to secure correct separation of quartz and opaline silica by the use of either caustic or carbonated alkalies; and that digestion on the water bath for fifteen minutes with 5 per cent solution of sodium carbonate is the only way to secure exact separation of unignited precipitated silica from quartz, and then only when the finest flour has been removed by levigation. The authors say:

If, however, no more of such flour is present than is produced in the ordinary operations of powdering and sifting through cloth of the finest mesh, the error arising from the above-mentioned treatment is so slight that it can generally be neglected; it reaches 0.1 to, at the most, 0.2 per cent of the total silica, by which amount the quartz will appear too low, the amorphous silica too high.

The above authors also show, however, that the solvent action of the caustic alkalies on quartz becomes very apparent only when the

¹ Zeitschr. angew. Chemie, 1897, pp. 393, 425.

material has been reduced to such an utterly impalpable degree of fineness as is practically never reached in the preparation of samples for rock analysis. For this reason I have no hesitation in recommending the employment of a dilute solution of sodium hydroxide when the silica separated by acid from one of several mineral constituents of a rock is to be estimated. Even when dilution is considerable, solution is almost immediate, and as soon as this is accomplished—the point being known by the change in appearance of the residue—the solution should be diluted with cold water and filtered at once. The difficulty met with in filtration may often be overcome by faintly acidifying, which has the added advantage of at once arresting any further action of the alkali. If the dilution is sufficient no separation of silica results from so doing. Very dilute acid should also be used for washing. Lunge, when using sodium carbonate, washes with hot carbonate solution to which alcohol has been added, thus obtaining clear filtrates.

B. Sjollema¹ regards diethylamine as suitable for the separation of amorphous silica from quartz and silicates in soils. He found that a 33 per cent boiling aqueous solution of the reagent dissolved 0.65 gram of amorphous silica practically wholly after eight hours' action and a 16 per cent solution within 1 per cent, whereas the solubility of quartz powder was only 1.2 per cent after two days.

¹ Jour. landw. Chemie, vol. 50, 1902, p. 371; abstracts in Jour. Chem. Soc., vol. 84, 1903, p. 241; Analyst, vol. 28, 1903, p. 123; Chem. Zeitung, Rep., 1903, p. 21.

CARBONATE ROCK ANALYSIS.

III.—INTRODUCTION.

31. QUALITATIVE COMPARISON OF CARBONATE AND SILICATE ROCKS.

The analysis of an ideally pure carbonate of any one metal is of great simplicity. The carbonates met with in nature occasionally approach but probably never fully reach this condition of purity, as when we find them in the form of well-crystallized mineral species, like calcite, magnesite, siderite, and cerusite. Even in such cases it is usually true that the crystals either contain included foreign matter to a slight extent or are composed of more than one carbonate in isomorphous mixture, and then the separation of the different metals may demand considerable skill and time. The great carbonate formations of the earth's crust are never of this simple character, however; even the most dazzling white marble contains other ingredients than calcium carbonate, and the degree of admixture may vary from almost nothing up to that indefinite point beyond which the rocks are not classified as limestones or dolomites, but rather as calcareous shales, calcareous sandstones, etc.

The matters other than carbonates which these rocks may contain are in the main original constituents, having been introduced at the time the carbonates were themselves deposited. They may consist of the detritus of earlier geologic formations in the form of sand or clay that has undergone little or no alteration in the subsequent passage of time, besides carbonaceous matter derived from the marine life existing during their formation. But besides these there may be found secondary minerals that have resulted from chemical transformation in the mass of the accumulated sediments, either with or without the powerful aid of dynamic forces like long-continued movements of the crust or the intrusion of hot igneous rocks. The metamorphism produced by these last agencies is often of a most profound character and may result in the production of a great variety of minerals altogether foreign to the original sediments. The metamorphism may have been accompanied by the introduction and incorporation of new material, but even in the contrary case all the chemical constituents of the original detrital foreign matter have necessarily become a part of the carbonate rock. These constituents are furthermore necessarily those common to silicate rocks of the earth's crust, hence the carbonate rocks differ qualitatively in no

essential respect from their silicate associates except as to the more common occurrence of carbonaceous matter; and a complete analysis of one of them involves most of the determinations and separations described in the first part of this work. The analytical procedure differs, however, in some respects, owing to the great preponderance in most cases of components easily soluble in the common mineral acids, which either renders it unnecessary to use an alkaline flux or enables the analyst to reduce its amount very materially, thereby simplifying subsequent operations. The analysis is further simplified by the occurrence in reduced amounts, as a rule, of those elements which most complicate the analysis of a silicate rock. Only in the very purest carbonate rocks are some of them nearly or entirely lacking, as silicon, aluminum, and the alkalis, but the minor constituents zirconium, barium, and strontium are often not present in readily determinable amount.

In the following pages the descriptions will apply especially to those large deposits of carbonate materials denominated limestones, magnesian or dolomitic limestones, and dolomites, many of which are of great and growing economic importance. For the purpose of the analyst an exact definition of these terms is of minor significance. Indeed, among geologists there has been no uniform rule for the delimitation of these rocks, and any rule made must be purely arbitrary, since there is absolutely no break in the series between limestones and dolomites. The last name applies strictly only to the equiatomic double salt of calcium and magnesium, $\text{CaMg}(\text{CO}_3)_2$, and by some it is held that this should be its only application. On the other hand, the opposite extreme has been approached by those who contend that all limestones with as much as 1 or 2 per cent of magnesium carbonate should be classed as dolomites. According to H. Ries¹ the most prevalent practice among geologists seems to be to call all limestones with from 5 to 18 per cent of magnesium carbonate magnesian limestones and the rest limestones or dolomites, according as their magnesium-carbonate contents lie below or above these limits. Some, however, while subscribing to the above definition of magnesian limestones, would and do call those rocks with from 20 per cent of magnesium carbonate up to the dolomitic ratio dolomitic limestones. F. W. Pfaff² calls limestones with 11 to 46 per cent of MgCO_3 dolomites, since these are common, while those with 7 to 11 per cent he says are very rare, if indeed they occur at all.

It has seldom been considered necessary to analyze the carbonate rocks with any great attention to detail. The majority of analyses

¹ Bull. New York State Mus. No. 44, 1901, p. 644.

² Neues Jahrb., Beil. Band 23, 1907, p. 529.

have been made with reference to their technical utilization and with determination of only the more important constituents. In such cases it has been a common practice to omit direct determination of the carbon dioxide and either to calculate its supposed amount on the basis of the total lime and magnesia found or to regard the loss on ignition as representing the carbon dioxide. The portion insoluble in hydrochloric acid has been frequently stated as silica. Any iron that may have been determined has been reported as Fe_2O_3 , water and carbonaceous matter have been overlooked entirely or neglected, as also titanium, phosphorus, and the rarer constituents, and sulphur has been reported almost uniformly as SO_3 . Such practice has repeatedly involved very gross errors of omission as well as of commission, which, though of little moment in many cases from the commercial point of view, detract much from the value of all these analyses in the eyes of the geologist intent on gaining an exact knowledge of an important formation and of the possible sources of metallic ore deposits of economic value, whether these last are residual soils resulting from the subaerial decomposition of limestone formations or whether they are deposits of the ores of lead, zinc, vanadium, etc., that have been formed beneath the surface by the agency of circulating waters.

32. MINERAL COMPOSITION OF CARBONATE ROCKS.

The chief mineral compounds entering into the make-up of the carbonate rocks are of course calcium carbonate for the limestones proper, with the double carbonate, the mineral dolomite, in increasing proportions through the magnesian limestones and dolomites; but it is the exception to find them free from other carbonates as essential components, chiefly those of iron and manganese, which are usually in isomorphous combination with the constituents of one or the other of the above minerals. The proportion of these is far less than that of the others but sometimes aggregates several per cent. When they predominate the rock is no longer a limestone but becomes an ore of iron or manganese.

Neglect to take account of these minor carbonate constituents is a frequent source of error in the statement of analyses, where it is very common to find reported as carbonates only calcium and magnesium, and perhaps a considerable amount of iron as Fe_2O_3 and manganese as one of its higher oxides, although it is practically certain that these must have existed in large part as ferrous and manganous carbonate. A careful determination of the carbon dioxide will often tell whether this is so or not, for it will perhaps be found in excess of that required for lime and magnesia. A negative result, how-

ever, is not to be taken as proof of the absence of iron or manganese carbonate or both, for very often a small portion of the magnesia may be in silicate combination, or in some formations there may be a little gypsum to claim a portion of the lime. This last is not likely to be the case in the average hard rock that is used for the manufacture of cement. In such the sulphur often reported as SO_3 is likely to come from iron pyrites and perhaps to a limited extent at times from carbonaceous matter. Hence it is easy to see that except in absence of iron and manganese it is not possible to ascertain the exact proportions of calcium and magnesium carbonates, and in some of the excepted cases it is possible only after separate analyses of the parts soluble and insoluble in dilute acid have been made.

The commonest sulphide in limestone formations is pyrite, though often its presence is obscured by its extremely fine state of division or by carbonaceous matter. In the metamorphosed limestones, especially those altered by intruded igneous bodies, other sulphides, as sphalerite and galena, are not uncommon, and these and still other sulphides may form important ore bodies or again give rise by oxidation to equally or even more valuable ores of a different sort. The strongly metamorphosed siliceous limestones, however, are seldom subjected to chemical analysis, especially for commercial purposes.

The siliceous components may be of the most varied character. Their names alone might fill a page. Suffice it to mention for the metamorphosed rocks garnet, vesuvianite, wollastonite, tremolite, diopside, the scapolites, tourmaline, apatite, and silica in the form of chert. Cherty limestones are extremely common, and their silica was doubtless introduced during metamorphism. The chief siliceous components of unmetamorphosed limestone rocks are, as said before, sand and a clay. The latter particularly, since it is a clay, carries water, and this fact is usually overlooked in ordinary analyses. The analytical statements may show no water, though clayey matter is present to a large extent. The sand may be largely or altogether quartz, or it may be composed in part of such other minerals as are commonly found in sands, like mica, garnet, and zircon. The latter may often be detected, even in the less siliceous and clayey limestones, by dissolving large amounts in hydrochloric or acetic acid and subjecting the residue to microscopic examination, after burning off obscuring carbonaceous matter, if necessary. The unignited residue will, needless to say, contain the pyrite of the rock and any other sulphides not attacked by dilute acid. In some nonsiliceous rocks it may even consist to a considerable extent of iron oxide, probably in most cases one of the hydrated oxides, but perhaps often hematite. The presence of such a constituent in a limestone is

occasionally indicated by a reddish cast of color in the fresh rock, provided there is not enough carbonaceous matter to obscure it. The existence of a ferric oxide is not always incompatible with the simultaneous presence of this carbonaceous matter.

A purple color may be due, as in some slates, to admixture of a ferric oxide or hydroxide with carbonaceous matter, while to the latter component are due the gray and black colors often encountered. The color of greenish sedimentary limestones may be caused by certain minerals of the mica family, as the chlorites.

The condition of phosphorus when it occurs in only minute amounts is not determinable with certainty. Doubtless it may be found sometimes in traces in the form of heavy phosphates like monazite and xenotime in the insoluble residues, and again it is held by iron and aluminum, but in the highly phosphatic rocks its usual form is overwhelmingly that of phosphorite or apatite, which may in fact become the predominating constituent.

It is known from my analyses that vanadium is a regular though very minor constituent of limestones as well as of sandstones and igneous rocks generally. Tests on 100-gram lots of a great limestone formation in northwestern Mexico show that it at least carries molybdenum as well as vanadium, and also nickel. Nothing is known with certainty regarding the mode of combination of these elements in limestones, though it is quite possible, as to the vanadium at least, that it was an original ingredient of the aluminous silicates of the clayey matter, and that nickel, zinc, and lead when present are mainly in the form of carbonate or sulphide.

Carbonaceous matter has been alluded to frequently as a common constituent of secondary importance. It is absent from the white marbles and some colored decorative stones but forms an appreciable percentage of other limestones in extreme cases.

Some kinds of bituminous limestone are characterized by a fetid odor when struck or abraded. This is perhaps due in most cases to hydrogen sulphide, either original or resulting from decomposition of organic matter. The presence of hydrogen sulphide is sometimes unmistakable, and B. J. Harrington determined its amount at about 0.02 per cent in the form of liquid inclusions in a fetid calcite from Canada.

The above remarks do not exhaust the subject of the mineral composition of limestone rocks, this term being used here and elsewhere in its generic sense to include the magnesian varieties. They may serve as a sufficient guide, however, to chemists undertaking the analysis of these rocks. Ignorance of the minor mineral components has been a prolific source of error in these analyses.

33. BEHAVIOR TOWARD DIFFERENT REAGENTS AS A MEANS OF DISTINGUISHING DIFFERENT CARBONATES.

Although for the analyst provided with laboratory facilities it is usually of little importance to possess other means for identifying qualitatively the different varieties of carbonate rocks than the conventional methods of qualitative analysis, some of the rapid methods for so doing may serve a most useful purpose at times, especially in the field, where transport of bulky apparatus and quantities of liquid reagents is difficult or impossible.

A. DIFFERING SOLUBILITY IN TARTARIC AND CITRIC ACIDS AND IN ACID POTASSIUM SULPHATE.

This subject, touched on now and then by earlier writers, was first studied by H. C. Bolton,¹ and many of his results were long afterward confirmed by J. W. Richards and N. S. Powell.² Solid organic acids like citric and tartaric were found to be well adapted for distinguishing between many carbonate minerals by the difference in the degree of action on them. Potassium acid sulphate had been used earlier to some extent by E. Jannettaz,³ and Richards and Powell give data as to this reagent for carbonates. It will suffice here to refer to the originals, especially Bolton's papers, where will be found data as to the solubility of a great variety of minerals in the above-named solvents as well as in others of inorganic nature.

B. DISTINGUISHING CALCITE FROM ARAGONITE.

In preceding editions of this work reference was made to chemical methods for distinguishing qualitatively calcite from aragonite. Since then other methods have been proposed. In the opinion of J. Johnston, H. E. Merwin, and E. D. Williamson⁴ these tests used alone are indecisive, "particularly so where they would be most useful, namely, for the characterization of fine-grained material which may carry something that interferes with the test." Hence their description is omitted from the present volume. Optical methods in experienced hands are more trustworthy.

C. DISTINGUISHING BETWEEN CALCITE AND DOLOMITE.

It must be understood that magnesian and dolomitic limestones represent, as a rule, mixtures of the double carbonate dolomite with

¹ Ann. New York Acad. Sci., vol. 1, 1877-1880, pp. 1, 153; vol. 2, p. 1; Proc. Am. Assoc. Adv. Sci., vol. 31, 1883, p. 271; Chem. News, vols. 36, 37, 38, 43, 47, 1877-1883; Rept. Brit. Assoc. Adv. Sci., 1880, p. 506; Mineralog. Mag., vol. 4, 1880-81, p. 181; Ber. Deutsch. chem. Gesell., vol. 13, 1880, p. 726.

² Jour. Am. Chem. Soc., vol. 22, 1900, p. 117.

³ Compt. Rend., vol. 77, 1873, p. 838; vol. 78, 1874, p. 852.

⁴ Am. Jour. Sci., 4th ser., vol. 41, 1916, p. 473. This article contains a summary of the literature upon the subject.



calcite, and not of calcite with magnesite. Calcite is easily soluble in dilute hydrochloric and acetic acids; dolomite and magnesite are nearly insoluble. Hence calcite effervesces strongly with these acids, even in lump form, while dolomite shows little or no effervescence. An easy means is thus afforded for distinguishing the two. Dolomitic limestones are also but feebly attacked, according to their content in calcite, so that in powder form it is not difficult to make a fair separation of calcite from dolomite and magnesite, but not from magnesian hydrocarbonates, which last, however, are never essential components of the great carbonate formations.

The behavior toward heat alone is sometimes useful as a distinguishing test, for dolomite loses its carbon dioxide so easily that the powder is violently projected from the crucible if the heat is not very cautiously applied, whereas calcite can be strongly heated at the start without danger of loss of solid matter.

J. Lemberg¹ found that calcite responds by the formation of a violet color in its powder when treated with a solution of aluminum chloride and hematoxylin (extract of logwood) but that dolomite remains unaffected. The solution is prepared by dissolving 4 parts of dry aluminum chloride in 60 parts of water, adding 6 parts of logwood, and boiling for 25 minutes with replacement of the escaping water. The deep-violet solution is then filtered.

Coarsely powdered Iceland spar and Carrara marble became violet after 5 to 10 minutes immersion and subsequent removal of the adhering solution with water. In the powder of a dolomitic limestone the calcite grains were easily distinguishable from those of dolomite by this means. It is not advisable to prolong the treatment unnecessarily, for after 20 minutes the dolomite surfaces may show occasional pale-blue spots. The reaction is caused by precipitation upon the calcite of aluminum hydroxide, which forms, with the coloring matter, a lake.

F. Hinden² finds that limestone (calcite) at room temperature gives carbon dioxide with 10 per cent solution of ferric chloride, but dolomite does so only on warming. A second reagent mentioned by him is copper sulphate solution, from which basic copper carbonate is separated by calcite, but is not by dolomite.

It is not known if objections similar to those mentioned in the foregoing section B, apply to the procedures of Lemberg and Hinden. The possibility, however, should be borne in mind.

¹ Zeitschr. Deutsch. geol. Gesell., vol. 40, 1888, p. 357.

² Verh. Naturforsch. Gesell. Basel, vol. 15, 1905, p. 1.



IV.—REFINED METHODS OF ANALYSIS.

34. SILICA, ITS SEPARATION FROM ALUMINA, ETC.

A. METHODS OF DECOMPOSING THE ROCK.

Few limestones are so pure that they leave no residue on treatment with hydrochloric acid. The residue may consist of quartz, clay, or other silicates, carbonaceous matter, pyrite, etc., and the mode of attack employed will depend on the amount of insoluble matter, and whether or not it is desired to know its composition separately from that of the soluble portion.

a. WHEN THE INORGANIC RESIDUE IS TO BE SEPARATELY ANALYZED.

A gram of the rock powder is moistened with water and dissolved in dilute hydrochloric acid (or acetic, if the former acid is likely to act appreciably on the silicates) in a covered beaker till all effervescence ceases. Moderate heat is needed if the effervescence is so weak as to indicate a rock of dolomitic character. The solution is filtered through a 7-cm. filter and the residue washed with water, or hot dilute hydrochloric acid should gypsum be present and the silicates resistant. The paper, with its contents, is ignited moist in platinum (blast needed only if the amount is considerable), and after weighing it is fused with sodium carbonate and analyzed like a silicate rock (6. A. d, pp. 94 et seq.). If it contains hydrous minerals the original water content of the residue is best determined by a separate test on a fresh portion of the sample and not by drying and weighing on a counterpoised filter and then igniting. The weight of water found should be added to that of the ignited residue in order to get the true weight of the insoluble matter.

If the ignited residue is wholly quartz, or is very insignificant in amount, it may be treated at once with a drop of sulphuric acid and a few drops of hydrofluoric acid, and the acids removed in the radiator shown in figure 2 (p. 33). If then a slight residue still is visible, it is well to repeat the treatment with acids and evaporation, for it can not be too insistently pointed out that quartz resists the action of hydrofluoric acid far more than many silicates, and several evaporations may be needed to volatilize the crystallized mineral unless it has first been reduced to a most impalpable state of division. When the weight after exposure for a few minutes to the full burner heat no longer changes, the loss represents silica. If a slight residue still shows

(it is most likely to be mainly alumina), the subsequently obtained precipitate of alumina, etc., is added to it and ignited in the same crucible. The filtrate is best treated as in 35. A. a, page 257.

If the original residue is small, and accurate knowledge of its composition is desired, several grams of the rock may be dissolved. In this case the whole filtrate from the insoluble matter is best treated for dissolved iron, aluminum, and manganese as in 35. A. a, page 257, but then only an aliquot part of the subsequent filtrate should be used for the determination of calcium and magnesium.

In case the filtrate from the residue is colored perceptibly by dissolved organic matter, a condition that may arise occasionally, this organic matter must be effectually destroyed before proceeding to the precipitation of iron and aluminum, for otherwise incomplete precipitation of one or both will be the result. The complete removal of this disturbing material can not always be effected by ordinary oxidizing agents, but only by evaporation and heating to its carbonization point. In doing this it is necessary, in order to avoid possible loss of iron as chloride, to evaporate with nitric acid to dryness a couple of times and then to heat over a free flame gently till the desired result is achieved. If this seems undesirable for any reason, it may be better to start with a fresh portion of the limestone and to treat it by one of the methods given under b, below, for the bulk analysis.

b. WHEN THE INORGANIC RESIDUE IS NOT TO BE SEPARATELY ANALYZED.

The usual case does not involve separate analysis of the inorganic residue. As said above, the residue may consist of clay or other silicates, carbonaceous matter, pyrite, etc., with or without quartz. There are two ways open to render the noncombustible part of this soluble.

a. By solution in acid after strong ignition.—Solution in acid after strong ignition is the best method to employ if the ratio of insoluble to soluble compounds is not less than that in an argillaceous limestone which is directly suited for burning to Portland cement—that is to say, if the silica does not much exceed 15 per cent and the oxides of iron, aluminum, and titanium together are not in excess of 6 per cent. The exact allowable limits have not yet been determined, nor is it known what the proportions may be in dolomites and dolomitic limestones. This is a subject for further investigation.

Limestones, however, in which the above percentages of silica, alumina, etc., are not exceeded may be converted in 10 to 15 minutes by a good blast capable of giving an effective temperature of 1,100° to 1,200° to a product that is wholly soluble in hydrochloric acid, provided the rock was first reduced to a very fine powder.

A gram of the powder is heated in a covered platinum crucible by an inclined blast. If a limestone, the flame may be applied at once, as a rule, without fear of loss, or after short exposure to a full Bunsen flame. Highly magnesian limestones, if this method is applicable to them, must, however, be heated with the greatest caution, for their temperature of decomposition is far below that of limestones, and violent projection of material often begins far short of visible redness.

The strong heating is usually stopped after 10 or 15 minutes, when the shrunken product may have the appearance of a sintered or even clinkered mass that detaches for the most part readily from the crucible.¹ It is transferred to a beaker or evaporating dish and moistened with water. The crucible is then cleaned with hydrochloric acid (1 : 1), and the contents are poured into the beaker or dish. By gentle heat and cautious pressure with the flattened tip of a rod the lump or lumps are caused to disintegrate and pass largely into solution in a few minutes. A certain amount of silica may remain undissolved in a flocculent state, but this is of no moment. When all grit has disappeared, the liquid, if in a beaker, is washed into a dish and evaporated to dryness. If solution was made directly in the dish the volume of liquid need not exceed a few cubic centimeters and the evaporation takes but a short time. A much smaller dish is allowable than in the case of wholly siliceous minerals, because of the small bulk of solution and the entire absence of added fixed salts.

β. *By solution in acid after heating with sodium carbonate.*—When the siliceous components are in such amount as not to permit the formation of a wholly soluble product by strong ignition, it is necessary to mix sodium carbonate with the powder and decompose the silicates by its aid over the blast lamp. This procedure may be adopted with all siliceous limestones if desired. The amount of flux to be used is but a fraction of that needed for a silicate analysis. One-fourth to one-half gram for 1 gram of limestone suffices,² for the lime formed by ignition is itself a powerful flux, and it is quite unnecessary to have here a liquid fusion. A sintering suffices. This proportion holds also for highly magnesian limestones and for cement rocks containing as little as 50 per cent of lime.³

¹ The changes that take place during the ignition comprise loss of all carbon dioxide, water, and carbonaceous matter; oxidation of all pyrite, with retention of the whole of the sulphur as calcium sulphate. Prolonged heating will gradually expel all the sulphur trioxide from the calcium sulphate and later the alkalies, which can be wholly volatilized in an hour or less by a powerful blast. With an inclined blast the alkalies condense in part on the under side of the lid as a soluble and powerfully alkaline deposit, sometimes weighing several milligrams, but in the time above set no loss of alkali appears to occur.

² Shimer, P. W., in Meade, R. K., *The chemist's pocket manual*, p. 162.

³ Personal communication from R. K. Meade.

B. SEPARATION OF SILICA.

In this connection the remarks under 6. B. a: β (p. 99) should be carefully read.

Because of the absence of large amounts of alkali salt and of much silica the evaporation of the hydrochloric acid solution obtained in A. a and b. α and β , takes little time as compared with a silicate analysis. When dry, or nearly so, on the steam bath, the dish may be placed in an air bath or (covered) on a platinum triangle resting on a hot plate, and heated to 200° for an hour if a limestone is under treatment, but for a highly magnesian limestone the temperature should not exceed 120°, according to J. P. Gilbert,¹ because of recombination of silica and magnesia, with subsequent re-solution of the silica when acid is added.

Bertram Blount claims² that by heating to 200° in this manner the silica is completely separated by a single treatment, but I have not found it so, though the amounts going into solution on subsequent addition of acid are small, seldom over 2 or 3 milligrams. Therefore, for exact work with silica present to the amount of 2 to 4 per cent and over, that already rendered insoluble should be filtered off and the solution again evaporated. With this end in view the dry mass is drenched with strong hydrochloric acid and allowed to stand for a few minutes, then as much water is added and the dish covered and placed on the bath for 10 minutes. Instead of strong acid that of half strength may be used and the heating begun at once. The silica is then separated by filtration on a filter of suitable size, washed thoroughly with dilute acid and then twice with cold water. The filtrate is evaporated again to dryness, the residue extracted with hydrochloric acid as before, but with allowance of only a few minutes' time and the solution filtered once more through a second and smaller paper. The two papers with their contents are slowly dried, charred, and ignited in platinum, finally over the blast for 10 minutes. The weighed silica is to be corrected for foreign matter by evaporating with 5 cm.³ of hydrofluoric acid and one or two drops of sulphuric acid, as directed in 6. B. c (p. 103). The residue obtained after ignition is almost always considerably less than that found in analyzing a silicate rock, and an ignition of a minute or two over a full burner, after expulsion of the sulphuric acid, is in almost all cases sufficient. The composition of this residue is similar qualitatively to that derived from silicate rocks. It should never contain calcium or magnesium but consists mainly of alumina, with a little ferric, titanic, and phosphoric oxides. It is preserved, and the subsequently obtained precipitate of these oxides is added to it and ignited in the same crucible.

¹ Tech. Quart., vol. 3, 1890, p. 61; abstract in Zeitschr. anal. Chemie, vol. 29, 1890, p. 688.

² Jour. Soc. Chem. Ind., vol. 21, 1902, p. 1217.

35. ALUMINUM, TOTAL IRON, TITANIUM (SILICA, MANGANESE); PRECIPITATION IN COMPANY WITH PHOSPHORUS.¹

The next steps differ widely according to the relative amounts of iron, aluminum, etc., taken collectively, and according as it is the intention to precipitate manganese with these or after separation from them. The individual preferences of experienced analysts will often differ as to the selection of the particular method, and it is not intended here to prescribe definitely the course that anyone should follow. Nor in the following paragraphs are all methods of separation that may be capable of affording good results noticed. There are some that seem promising but that have not yet been studied sufficiently in the Survey laboratory, nor in fact elsewhere, to justify description. A method that may be well adapted to a certain combination of elements may be valueless if to that combination a single other element is added; or it may be that the possible disturbing influence of that element has not yet been ascertained.

A. PRECIPITATION OF ALUMINUM, IRON, ETC.**a. COLLECTIVE PRECIPITATION OF ALUMINUM, IRON, MANGANESE, TITANIUM, AND PHOSPHORUS BY AMMONIUM SULPHIDE.**

If aluminum, iron, manganese, titanium, and phosphorus collectively represent 2 or 3 per cent or less of the rock, the filtrate from the silica (34. B, p. 256), reduced in bulk if need be, is put into a flask of 150 cm.³ capacity with enough hydrochloric acid to prevent precipitation of magnesium when made ammoniacal. This last is a most important point. Ammonia free from carbonate is then added to strong alkalinity and hydrogen sulphide is introduced to saturation, followed by a fresh addition of ammonia equal to the excess first used. Boiled water is then poured in till well up in the neck, the cork is inserted, and the flask is set aside for 12 to 24 hours. Its contents are then collected on a filter of small size (7 cm.) and washed with water containing a little ammonium sulphide and chloride. Precipitation is not absolute as to one or more of the constituents of the separated mixture, but the amounts recoverable from the filtrate are usually very minute. (For treatment of the filtrate, see 38, p. 262.)

The paper and its contents, having been washed with ammonium chloride, may be safely charred and ignited as they are, in the crucible containing the residue left after volatilizing the silica. The final weight after ignition in full contact with air, followed by application of the inclined blast for not over 5 minutes, represents Al_2O_3 , Fe_2O_3 , Mn_3O_4 , TiO_2 , and P_2O_5 . (For the separation of these, see C, p. 259.)

¹ See also section 8, p. 106.

This method is inapplicable for phosphatic limestones containing insufficient aluminum to more than combine with the phosphorus, for then calcium phosphate would be precipitated also. In such case method b or c would apply if the iron and aluminum together more than sufficed to carry down the phosphorus, but in general it would be necessary to add a known amount of pure iron oxidized to the ferric state, then to precipitate by ammonia or the basic-acetate process, and to deduct the added iron oxide from the weight obtained.

D. PRECIPITATION OF ALUMINUM, IRON, TITANIUM, AND PHOSPHORUS BY AMMONIA.

The filtrate from silica is boiled in a beaker of good glass, with addition of a few drops of bromine water or two or three drops of strong nitric acid, till all trace of bromine or chlorine is gone. Then hydrochloric acid is added, if not already present, in amount sufficient to prevent precipitation of magnesium when rendered ammoniacal. A few drops of methyl red solution are added and the liquid (100 to 200 cm.³ in volume) is heated just to boiling. Neutralization is then brought about by means of ammonia (dilute toward the end) until the color of the solution changes to a distinct yellow. It is then boiled for 1 or 2 minutes, allowed to settle, filtered, then at once washed two or three times with hot ammonium chloride solution (2 per cent), and sucked dry. (Consult 8. B. a. β , p. 107.) The precipitate is then redissolved in hot and moderately strong hydrochloric acid, the solution is boiled to drive out the trace of chlorine derived from solution of any precipitated manganese dioxide, and the precipitation is repeated one or more times just as described, according to the amount of manganese in the rock. Macerated filter paper is added before the last precipitation if the oxides are in large amount. The final precipitate is washed with water containing a little ammonium chloride. (For treatment of the filtrate, see B, below.)

The precipitate is ignited moist in the crucible containing the residue from volatilization of the silica by hydrofluoric acid, and the combined weights increased by traces subsequently recovered (B, below) represent all iron as Fe_2O_3 , Al_2O_3 , TiO_2 , and P_2O_5 . (For separation of the ignited oxides, see C, p. 259.)

C. PRECIPITATION OF ALUMINUM, IRON, TITANIUM, AND PHOSPHORUS BY THE BASIC-ACETATE METHOD.

The basic-acetate method of separation is less employed in limestone analysis than in that of silicate rocks, by reason of the relatively smaller amounts of those elements that precipitate in the basic-acetate process, and hence of their more ready separation by ammonia from appreciable quantities of manganese. (For its application, see 8. B. b. β , p. 110, giving due regard to the smaller amounts of iron, etc., involved in the case of limestones.)

B. TREATMENT OF THE FILTRATES FROM ALUMINA, ETC.

The combined filtrates obtained in A. b (or c), above, which, besides all the calcium and magnesium, will contain the manganese and usually traces of aluminum and even iron, are evaporated to a small volume in platinum with the addition of a few drops of ammonia from time to time, and any precipitate that separates is collected. This is washed a little, redissolved in hydrochloric acid (with addition of a drop or two of sulphurous acid if its color indicates precipitation of some manganese), and reprecipitated by ammonia at boiling heat in a very small beaker. If need be the precipitation is to be again repeated, but this will seldom be the case. A first precipitation is, however, called for in order to separate a little calcium carbonate that may have precipitated during the evaporation of the original ammoniacal filtrate. The alumina and perhaps trace of iron oxide thus obtained are added to that already found (A. b or c, p. 258). (For treatment of the filtrate, see 36, p. 260.)

C. SOLUTION AND SEPARATION OF THE OXIDES OBTAINED IN A AND B.

The same course is followed, whether method a, b, or c under A (pp. 257-258) has been employed for precipitating aluminum, iron, etc. According to the weight of the ignited oxides, these are fused with from one to several grams of potassium or preferably sodium pyrosulphate¹ in the covered crucible over a low flame. By using pyrosulphate instead of acid sulphate the time of fusion is greatly shortened, especially when the oxides are in a finely divided state, as after precipitation in presence of macerated filter paper.

When decomposition is complete the cooled melt is dissolved in hot dilute sulphuric acid, the solution is transferred to a capacious platinum dish and evaporated as far as practicable on the bath. Strong sulphuric acid is cautiously added, and evaporation is continued over a radiator, or on a sand bath, or by aid of a free flame applied with care to prevent spattering, till fumes of acid appear freely. When cool, the melt should be rather pasty and not hard and dry. It is dissolved by the aid of heat in a moderate amount of water, and the solution is allowed to digest for 10 to 15 minutes on the bath. A few flocks of silica will then generally be apparent at the bottom of the dish. Whether visible or not, the solution is passed through a 7-cm. filter, which is then washed with hot water till free from salts.

a. SILICA (BARIUM).

The paper with the silica is ignited, weighed, and then treated with a drop of sulphuric acid and a few drops of hydrofluoric acid and the crucible, after ignition, is again weighed. The loss represents silica that escaped earlier separation, and its amount is to be added to that already found.

¹ For its preparation see p. 46.

If a final residue is reddish, it is to be brought into solution by a little pyrosulphate and its solution, if clear, added to the main filtrate containing the mass of the iron. If not clear, the turbidity may be due to a trace of barium sulphate, which should of course be separated and deducted from the weight of the alumina plus other oxides.

b. IRON.

In this solution the iron is to be determined by potassium permanganate after reduction by hydrogen sulphide, exactly as detailed under 9. C. a (p. 119). The amount of vanadium present is, so far as known, always so small as to make it unnecessary to follow the procedure under 9. C. b (p. 121).

c. TITANIUM.

After titration of the iron the solution is treated exactly as prescribed under 9. C. a. β (p. 120), and the titanium is determined colorimetrically (p. 155).

d. ALUMINUM.

The aluminum is determined by difference after subtracting the weights of iron and titanium oxides found as above, and also the phosphoric oxide found in a separate portion of the sample (39, p. 263), and further the manganoso-manganic oxide, if this had intentionally been precipitated along with the iron and aluminum as in A. a (p. 257). (For the discussion of the relative merits of this indirect and the direct methods for arriving at the aluminum, see 9. A, p. 115, and 10. A, p. 126.)

36. MANGANESE.

A.—IN THE FILTRATES FROM 35. B.

The filtrates containing the calcium, magnesium, and manganese are caught in a flask of about 150 cm.³ capacity, 2 cm.³ of ammonia is added, and hydrogen-sulphide gas is introduced to saturation, then additional ammonia is added to equal that just prescribed. The flask is stoppered and set aside for 12 to 24 hours, the precipitate (perhaps colored dark by a little platinum, iron, or other heavy-metal sulphide¹) is collected on a 7-cm. filter and washed with a dilute solution of ammonium chloride carrying a little ammonium sulphide.² (For treatment of the filtrate, see 37, p. 261.)

¹ More than a negligible trace of iron should not appear at this point. If, however, the organic matter of the limestone is at all soluble in acids and the method of direct solution has been employed, it may very well happen that some iron (aluminum likewise) will fail of precipitation by ammonia. The former will then appear at this stage. Hence, prior ignition of the limestone is imperative in such cases.

² This is best prepared by considerably overneutralizing a little hydrochloric acid in a small beaker, and then adding hydrogen sulphide water or introducing hydrogen sulphide gas for a few moments, and further diluting if need be.

If the manganese is not to be determined in a separate portion of the rock, the flask is then cleaned from possibly adhering sulphide with a solution of half-strength hydrochloric acid diluted with five times its volume of hydrogen sulphide water, which is then passed through the filter in order to dissolve the manganese sulphide. The filtrate is treated exactly as under 11. B. b (p. 136), if the gravimetric method of determination is chosen. In view of the relatively enormous errors affecting this method when small amounts are in question (see 11. A, p. 134), it is far safer to evaporate the hydrochloric acid solution with nitric or sulphuric acid, till no trace of chlorine is left, and to apply the colorimetric method (11. C. b, p. 137).

If the manganese is to be determined in a separate portion, the sulphide precipitate is discarded; indeed, if it is known that but a few hundredths of 1 per cent are present, its separation at this stage may be altogether omitted.

B. SEPARATE DETERMINATION OF MANGANESE.

Small amounts of manganese are always determined best by colorimetry, and then with greatest accuracy in a separate portion of the sample. This, if wholly soluble in acid, is to be dissolved by dilute nitric acid free from hydrochloric acid, the solution filtered if necessary, and further treated, in whole or in an aliquot part, as in 11. C. b (p. 137). If not altogether soluble in acid or if the solution is colored by organic matter, it is best to heat the powder with half its weight of sodium carbonate (itself free from manganese) over a strong blast, to digest the cooled mass with nitric acid till any residue that may remain is entirely colorless, to filter into a suitable-sized flask, and to determine as in 11. C. b (p. 137).

37. COPPER, NICKEL, COBALT, LEAD, ZINC, RARE EARTHS, CHROMIUM, VANADIUM, MOLYBDENUM.

It is commonly useless to look for copper, nickel, cobalt, lead, zinc, rare earths, chromium, vanadium, or molybdenum in a sample so small as that taken for the general analysis. To detect these from 50 to 500 grams of material will be required, which should be dissolved in hydrochloric acid and the residue separated by filtration. If it is desired to examine this residue, it is analyzed separately, after fusion with sodium carbonate and leaching with water. Chromium, vanadium, and molybdenum will then be found in the filtrate, the other metals in the residue. The former can be determined according to 20 (p. 184); the latter by the usual methods.

For the hydrochloric acid solution, which will contain the above elements mainly or wholly, the treatment given under 35. A. a

(p. 257), is probably best adapted, and the following outline may serve as a guide:

The precipitate produced by ammonium sulphide is to be dissolved, the copper and perhaps some molybdenum precipitated by hydrogen sulphide, the filtrate oxidized and evaporated to dryness, and the residue boiled with a solution of oxalic acid. The rare earths, perhaps contaminated by silica, will be thrown out and are to be washed with dilute oxalic acid solution, ignited, treated with sulphuric and hydrofluoric acids, redissolved, and reprecipitated in neutral or nearly neutral solution by oxalic acid, ignited, and weighed. They can then be tested as to their character by methods to be found in special treatises on the rare earths. The filtrates are freed from oxalic acid by evaporation and gentle ignition and the residue is redissolved and tested for nickel, cobalt, zinc, chromium, vanadium, and molybdenum by approved methods. It must not be forgotten that the filtrate from the original precipitation by ammonium sulphide may hold most of the vanadium and molybdenum, and perhaps nickel, which are to be recovered by acidifying with dilute acetic acid.

Vanadium may usually be found and determined with sufficient accuracy in 5 grams of the limestone by fusing with sodium carbonate and further treating as in 20. C (p. 185).

38. CALCIUM, STRONTIUM, BARIUM, MAGNESIUM (MANGANESE).

A. ORDINARY PROCEDURES.

The filtrate obtained in 35. A. a (p. 257), or 36. A (p. 260), is treated for the most part as in silicate analysis (pp. 135-153).

With dolomitic limestones and dolomites it will be usually impossible to obtain a correction by the method given in 13. C. b. β (p. 152) for the small amount of calcium with the magnesium pyrophosphate. The first of the methods there given (α) is to be followed.

The accurate determination of barium in a limestone is more difficult than in a silicate rock. It is perhaps best to recover it, if present, from the filtrates from the calcium oxalate, after evaporating them and expelling ammonium salts, by taking up the residue in as little hydrochloric acid as possible and, without filtering, adding a few drops of sulphuric acid and allowing to stand for several hours. The washed and ignited precipitate is evaporated with a drop of sulphuric acid and a few drops of hydrofluoric acid to remove silica, the final residue is dissolved by a little hot strong sulphuric acid, and the resulting solution poured into a few cubic centimeters of cold water, the crucible being well rinsed with cold water by the aid of a feather or "policeman." If a precipitate now appears it is barium sulphate, which is collected and weighed in the customary manner.

To the filtrate is added enough hydrochloric acid to prevent precipitation of magnesium when rendered ammoniacal. Ammonia in slight excess is added and the solution is boiled for some minutes in a platinum dish. There will probably appear a very slight precipitate containing aluminum hydroxide, which is to be redissolved and reprecipitated. In the filtrate the magnesium is precipitated, together with any manganese that may be present, in the manner elsewhere detailed (13. A, p. 148).

B. SEPARATION OF LITTLE CALCIUM FROM MUCH MAGNESIUM—MAGNESITE ANALYSIS.

In section 12, under A. d (p. 142) are given procedures which appear to be the best for separating little calcium from much magnesium, as these occur in the commercially important mineral magnesite and its product of calcination. A method of F. Hundeshagen¹ has been condemned by Kallauner and Preller,² but in the light of what is said in section 12. A. d, the practiced analyst may perhaps be able to adapt the procedure to the complete analysis of magnesite or of any mineral that carries a great deal of magnesium and very little calcium.

39. PHOSPHORUS.

In determining phosphorus the rock is dissolved in dilute nitric acid, the solution filtered, the residue fused with a little sodium carbonate, and its nitric acid solution added to the other.

Or, if the rock is rather argillaceous, the powder may be mixed with half its weight of sodium carbonate and strongly blasted. The nitric acid solution of the mass is then evaporated to dryness to remove most of the silica, which is collected on a filter, washed, ignited, and evaporated with hydrofluoric and nitric acids. The evaporation with nitric acid alone is repeated once or twice to expel the fluorine, and the residue is dissolved finally in nitric acid and its solution added to the former.

To the solution obtained in either of the above ways ammonium molybdate solution is added, and the precipitate is treated by one of the approved methods.

In limestones very low in phosphorus it may be deemed desirable to concentrate the phosphorus from a considerable weight of sample. F. Hinden³ suggests the following way to do this:

To the nitric acid solution add ammonia until the liquid becomes slightly turbid. (Add a few drops of ferric chloride solution if

¹ Zeitschr. öfterntliche Chemie, vol. 15, 1909, p. 85.

² Chem. Zeitung, vol. 36, 1912, p. 462.

³ Zeitschr. anal. Chemie, vol. 54, 1915, p. 214.

iron and aluminum are absent.) Then add half a gram of pure precipitated calcium carbonate and boil for five minutes. Filter, dissolve the precipitate in dilute nitric acid, and precipitate the phosphorus as phosphomolybdate.

40. FERROUS IRON.

The presence of carbonaceous matter in limestones renders the exact or even approximate determination of ferrous iron often impossible. Nevertheless, even in its presence acceptable results are sometimes obtainable if there is not much of such matter and if it does not give with acid a colored solution. But even then it is only the soluble iron, existing chiefly if not wholly as carbonate, that is determinable. Occasionally limestones show films of manganese peroxide, which likewise interferes with the determination.

A. IN THE ABSENCE OF CARBONACEOUS MATTER.

a. FERROUS IRON SOLUBLE IN SULPHURIC ACID.

The powder, 1 gram to several grams, is introduced into a stout flask of about 200 to 250 cm.³ capacity and boiled with a little water till all air is expelled. While still boiling, dilute sulphuric acid is added, a little at a time, till effervescence ceases, and then a further amount. Calcium sulphate precipitates, but the iron will remain in solution. The flame is then removed and a stopper tightly inserted, through which passes a small stopcock funnel. When cool or nearly so, cold water is poured into the funnel, the cock cautiously opened, and the water drawn into the flask, more water being poured into the funnel as fast as it empties, till the solution amounts to 100 or 150 cm.³ Such precaution to exclude air is hardly necessary in most cases, however, for in presence of sulphuric acid the oxidation of ferrous iron is exceedingly slow. It is ordinarily quite sufficient to equalize the internal and external pressures by opening the cock, removing the stopper, and pouring in cold water. The flask is then brought under a burette containing dilute permanganate solution and the iron titrated without delay. With a carbonate which is wholly decomposable without the aid of heat, solution may be accomplished in a flask filled with carbon dioxide, using cold acid, whereby the danger of attack of silicates is lessened if these are present. If the preference is for the potassium-bichromate method of titration, hydrochloric acid may be used instead of sulphuric, in absence of manganese peroxide. In this case there is, of course, no separation of an insoluble calcium salt, a fact which renders easier the subse-

quent determination of the iron in any insoluble residue the rock may yield. The ferrous iron thus found is mostly, if not altogether, that existing as carbonate.

D. FERROUS IRON IN THE INSOLUBLE RESIDUE.

The titrated solution is filtered through a medium-sized hardened filter, the insoluble matter collected thereon and washed with water. The contents of the paper are rinsed into a capacious platinum crucible, the water mostly evaporated, and in the residue the ferrous iron is determined as in 21. D. d (p. 203).

The total ferrous oxide found in a and b, when calculated to ferric oxide and subtracted from the total iron in the same state, gives the ferric oxide in the rock. If separate analyses have been made of the parts soluble and insoluble in dilute acid, similar calculations applied to the iron derived from the two portions will give the ferric oxide in each.

C. TOTAL FERROUS IRON.

If separate determinations are not desired, water is poured upon the powder in a capacious platinum crucible, dilute sulphuric acid is slowly added till effervescence ceases, then the crucible is placed in one of the forms of apparatus described in 21. D. d (p. 203), together with 5 cm.³ of hydrofluoric acid, the decomposition of the silicates is effected in an atmosphere of carbon dioxide, and the titration is made as there directed.

B. IN THE PRESENCE OF CARBONACEOUS MATTER.

Decomposition is effected in a flask by dilute sulphuric acid in an atmosphere of carbon dioxide. With limestones and active agitation no heat need be used, but with dolomites it will be necessary. The solution is then filtered quickly through asbestos (in an atmosphere of carbon dioxide if much iron is present), the residue and filter washed a few times, and the filtrate titrated at once with permanganate. If it is colored by organic matter, the result may be in error.

As in 40. A. a (p. 264), hydrochloric acid and titration by dichromate may be used in the absence of manganese peroxide. In either case it is important to allow the acid to act no longer than is necessary and to filter quickly. A determination of the ferrous iron in the insoluble matter is usually not worth attempting, because of the admixed organic matter.

41. ALKALIES.

The alkalies in carbonate rocks are, of course, constituents of the siliceous components. As these are usually subordinate, it is advis-

able to operate on not less than 1 gram of the powder, and the J. Lawrence Smith method is to be followed in nearly all its details (22, p. 207). Because of the presence of a large amount of calcium carbonate in the rock it might seem that addition of precipitated carbonate would be needless. That it is not, however, appears to have been shown by experiments made with and without its addition. A little more alkali was obtained in the former case, a result that is probably due to more effective reaction of the finely divided artificial carbonate than of the crystalline natural carbonate with the ammonium chloride. One-half the usual amount of precipitated carbonate will suffice.

42. CARBON DIOXIDE, CARBON (WATER).

A. DETERMINATION OF CARBON DIOXIDE.

The determination of carbon dioxide is made precisely as under 23. B (p. 217). If the absorption tubes have a height of about 10 cm. and a diameter of 1.2 cm. the first one will need refilling after every second analysis. For this reason Liebig or Geissler bulbs containing potash solution may be preferred.

B. DETERMINATION OF CARBON OF CARBONACEOUS MATTER.¹

The character of the carbonaceous matter in limestones has not been made the subject of study, so far as known to me, but it seems reasonable to assume that it resembles coaly matter rather than the indefinite humus. Although on solution of the rock in dilute acids the odor of the escaping gas is sometimes indicative of volatile organic substances, the amount thus escaping can never be more than a small fraction of the total. If the rocks are boiled with acid the filtrate may be somewhat colored, but if care is taken to use dilute acid and to filter as soon as its action on the carbonates is over, little or no organic matter is likely to pass into solution. Hence, in all such cases the following method for the determination of its carbon is indicated, provided sulphides are practically absent:

Treat 1 to 10 grams of the rock with dilute hydrochloric acid till the carbonate constituents are surely decomposed, filter through an asbestos plug filling a constriction in a glass combustion tube, wash thoroughly with water, dry, and burn the carbonaceous matter over an ordinary burner in an air or oxygen current, collecting the escaping water in a calcium-chloride tube and the carbon dioxide in one

¹ Since this text was written a paper has appeared upon the determination of combustible matter in silicate and carbonate rocks which takes account of the hydrogen as well as the carbon of the organic matter. (Fieldner, A. C., Selvig, W. A., and Taylor, G. B., Tech. Paper Bur. Mines No. 212, 1919.)

filled with soda lime. The combustion need occupy but a few minutes as a rule.

If the rock is free from hydrous minerals, if the asbestos likewise yields no water on ignition, and if the asbestos and its load have been thoroughly dried, from the gain in weight of the calcium chloride tube the hydrogen of the organic matter may be calculated. These conditions will, however, seldom be fulfilled, so that only the carbon has to be considered. In fact, it is quite useless, ordinarily, to attempt to determine the organic matter as such, either directly or by calculation. One must perforce be content with knowing its contained carbon.

C. SIMULTANEOUS DETERMINATION OF WATER AND OF TOTAL CARBON.

In presence of sulphides or soluble organic matter the following method will sometimes answer for the simultaneous determination of water and of the carbon of carbonates and organic matter.

Ignite in a current of air 1 gram of the rock in a tube of very hard glass, or in the tubulated crucible of Gooch (fig. 16, p. 85), collecting the water and the carbon dioxide as in B. The sulphur of sulphides will be retained as calcium sulphate. It is necessary for the success of this operation that the temperature be sufficient to drive out all carbon dioxide from the carbonates, but insufficient to decompose calcium sulphate. The water found represents that in the minerals of the rocks as well as that derived from the hydrogen of the organic matter.

A separate determination of the carbon dioxide (see A, p. 266) gives the data for calculating the carbon of the organic matter.

According to G. T. Morgan¹ the two conditions of carbon can be determined successively on the same portion of sample by first finding the carbon dioxide as in A, but with substitution of orthophosphoric for hydrochloric acid, and then, after weighing and replacing the absorption tubes, adding chromic acid and renewing the boiling to oxidize the organic matter and liberate its carbon as CO₂.

43. CHLORINE.

Several grams of the rock is dissolved in the cold, or with as low a heat as may be, in dilute nitric acid free from chlorine, the solution is filtered, silver nitrate added, and the precipitate collected and treated as usual. (See 24. A, B, and C, pp. 220-221.)

If the rock is likely to contain chlorine-bearing silicates, it is decomposed with its own weight or less of chlorine-free sodium carbonate in a platinum crucible over the burner or moderate blast without undue prolongation of the heating. The mass is extracted with

¹Jour. Chem. Soc., vol. 85, 1904, p. 1001.

hot water and the filtrate acidified with cold dilute nitric acid, or it may be decomposed directly with the acid and the solutions filtered. The further treatment is as above given.

44. FLUORINE.

As with silicate rocks, an exact determination of fluorine in carbonate rocks is difficult if not impossible with our present methods, and little or nothing has been done along this line.

Because of the great preponderance of lime, direct fusion with sodium potassium carbonate and silica is of somewhat doubtful practicability. Probably the following treatment will afford the best results:

Dissolve the powder in dilute acetic acid, as far as this may be possible without boiling, and filter. To the filtrate add a solution of sodium carbonate till in some slight excess, boil, and treat the precipitate of calcium carbonate and possible fluoride as described on page 224. Most of the fluorine that may have been dissolved by the acetic acid will thus be found. The siliceous matter insoluble in acetic acid is fused with sodium-potassium carbonate and further treated as in 25. B. a (p. 222).

45. SULPHUR.

A. TESTS AS TO ITS CONDITION; DETERMINATION OF SULPHATE SULPHUR.

In very many, perhaps most, carbonate rocks any sulphur present is chiefly if not wholly in the sulphide condition, and then usually as pyrite. In what condition it may be is readily ascertainable. If moistened lead-acetate paper is blackened when held over the mouth of a test tube in which some of the rock powder is being boiled with dilute hydrochloric acid, a soluble sulphide is indicated, but it is seldom more than a negligible trace. If the filtrate after approximate neutralization with ammonia gives a precipitate with barium chloride there is sulphate present. If the total sulphur obtained as in B, below, is in excess of that in the sulphate and soluble-sulphide states, the difference may safely be calculated to iron disulphide.

In the presence of much sulphide and also of sulphate sulphur the extraction of the latter should be made in an atmosphere of carbon dioxide, but usually this precaution is quite unnecessary. For details of the determination of sulphur consult section 26 (p. 230).

B. DETERMINATION OF TOTAL SULPHUR.

a. METHODS OF CONVERTING SULPHIDES TO SULPHATES.

α. By ignition without flux.—In a rock that is not heavily charged with sulphides the following method of my own has afforded excel-

lent results, even in the presence of 1 per cent of organic matter, though its range of application has not been ascertained:

The platinum crucible containing 1 or 2 grams of the rock powder is placed in the perforated disk (fig. 3, p. 34) and exposed to the heat of a burner for fifteen minutes or to that of an inclined and moderate blast for ten minutes. So far as present experience teaches, it is not at all necessary to begin with a gentle heat. All sulphide sulphur is oxidized and retained by the lime as sulphate without any loss by volatilization, all organic matter is removed, and the silicates are rendered soluble in acid if they are not in excess. (See 34 A. b. α , p. 254.)

β . *By ignition with sodium carbonate.*—From 1 to 2 grams of powder is mixed with half the weight of sulphur-free sodium carbonate in a platinum crucible and heated in the perforated disk, as in α . It is not probable that the addition of niter is called for, even when a good deal of carbonaceous matter is present. Since not enough flux is used to produce more than a sintering, the air entering the crucible after the bulk of the carbon dioxide has passed off effects very speedy oxidation in the porous mass.

With highly impure limestones it may be necessary to increase the amount of flux and to use a little niter as well.

b. TREATMENT AFTER IGNITION.

The ignited mass obtained in a. α or β will usually separate easily from the crucible. It is transferred to a small beaker and covered with water. The crucible is cleansed with dilute hydrochloric acid and the solution poured into the beaker. More acid is added till decomposition is complete in the cold or on gently warming. The solution is then filtered, diluted if need be to 150 or 200 cm.³, brought to boiling or simply placed on the steam bath, barium chloride added, and the precipitated sulphate collected in due time and weighed as usual.

Evaporation to dryness to separate the dissolved silica is quite unnecessary. After decomposition with acid the solution should never be permitted to gelatinize, and it needs but little practice on the part of the operator to insure unfailing success in preventing this. If it should happen, however, it is generally best to begin over, but the difficulty may be overcome if but little free acid is present by dissolving the gelatinized silica in sulphur-free fixed alkali and reacidifying in the cold with hydrochloric acid.

46. WATER.

A. HYGROSCOPIC WATER.

From one to several grams of the air-dry powder is heated in a current of air dried by calcium chloride in a glass tube at 100° to

105° and the escaping water is collected in a calcium chloride tube, or the air may be dried by sulphuric acid and the water collected in sulphuric acid. This direct determination of the water is certain to give a higher and more correct result than that obtained by drying in a crucible at the above temperature.

B. FIRMLY HELD WATER.

Combined water may be determined ordinarily on the air-dry sample by heating in a tube of combustion glass and collecting the water in a calcium chloride tube with the above-mentioned precautions. Or the powder may be mixed with dry sodium carbonate and heated in the apparatus of Gooch (5. C. f, p. 85). From the result thus found the separately determined hygroscopic water is to be deducted. It is to be remembered that the result will be in error by the amount of water afforded by the hydrogen of any organic matter there may be in the limestone.

V.—CONDENSED ANALYSIS.

For many purposes, especially those with a technical end in view, a highly refined or detailed analysis is not called for. The analyses of this kind that are now made vastly exceed in number those demanding the kind of work provided for in many of the sections of Part IV. To meet the needs of those having work of this kind to do, a procedure is here given in brief that covers the important constituents of limestones. The operations are generally given without explanations. Those who seek reasons for one or another procedure or details of manipulations are referred to the corresponding sections of Part IV.

47. DECOMPOSITION AND SOLUTION.

If the substance is convertible by blasting into a condition wholly decomposable by hydrochloric acid, 0.5 to 1 gram of the fine powder is strongly ignited in a covered platinum crucible over the blast for 15 minutes, or longer if the blast is not very powerful.

If the material is very impure, 0.5 to 1 gram is to be mixed with half its weight of pure sodium carbonate and ignited over the burner and blast till well sintered together.

The ignited material obtained in either of the above ways is transferred to an evaporating dish, preferably of platinum, and moistened with a few cubic centimeters of water. The crucible is cleaned with dilute hydrochloric acid, the solution poured into the dish, which is to be kept covered if sodium carbonate was used, and more acid added. Solution of the mass may be aided by gentle pressure with the flattened end of a glass rod. The solution is then evaporated to dryness on the steam bath. It will do no harm with limestones low in magnesium to hasten dehydration of the silica by placing the dish with its dry contents in an air bath at an elevated temperature or on a triangle resting on a hot plate at 200° for an hour or less.

48. SILICA.

The residue is treated with 5 to 10 cm.³ of strong hydrochloric acid, which is then diluted to half strength, or upon the residue may be poured at once a larger volume of acid of half strength. The dish is then covered and digestion allowed to go on for 10 minutes on the bath, after which the solution is passed through a 7-cm. paper and the silica washed with water, cold at first and hot later, or with hot dilute hydrochloric acid at first, followed by a little hot water. The filtrate is again evaporated to dryness, this time only on the steam bath, after which the residue is digested with acid as before, but in smaller amount, and the second portion, of usually dark-col-

ored silica, is collected on another small paper. The filter papers with their contents are slowly charred in a platinum crucible, then ignited, first over the burner, finally over the blast for 5 to 15 minutes, according to the amount of the silica. If the blast is weak, a second application of it should follow the first weighing. The finally weighed silica is moistened with water, and two drops of sulphuric acid and 5 to 10 cm.³ of pure hydrofluoric acid are added, the crucible is placed in a radiator (fig. 2, p. 33), and the liquid wholly evaporated. The residue is blasted for a minute and in due time weighed. It is better not to make this correction if it is not intended to separate and determine also the silica always accompanying the iron and aluminum oxides, for the reason that with the small amount of silica in limestones the nonvolatile residue compensates more or less for the silica remaining in solution after the second evaporation; but it should never be omitted if this latter correction is contemplated.

49. ALUMINUM, IRON, ETC.

The filtrate, which need not exceed 100 cm.³ in bulk with fairly pure limestones, is brought to boiling in a beaker, or preferably in platinum, and made alkaline with ammonia after adding a few cubic centimeters of bromine water, and if need be enough hydrochloric acid to insure a total of 10 to 15 cm.³ of strong acid. The ammonia should not be in such excess as to require long boiling to expel the most of it, nor is the expulsion of the whole of it necessary or indeed desirable. As soon as the precipitate settles, the solution is passed through a filter of suitable size and the precipitate is washed a few times with hot water and sucked fairly dry. It is redissolved in hot hydrochloric acid and precipitated again by ammonia in presence of bromine, but with less ammonium chloride and in a smaller bulk of solution. If the filter is still in good condition, it is used also for this precipitate, which is washed with hot water and sucked dry at the pump. With high iron and magnesium the precipitation may well be repeated.¹

The re-solution of the first precipitate may be made with nitric acid, if thought desirable. Its use involves very little washing of the second precipitate. To reduce the amount of aluminum passing into the filtrate, the precipitated oxides may be washed with water containing in the liter 20 cm.³ of nitric acid that has been neutralized with ammonia.

The paper containing the final precipitate is placed in a platinum crucible, slowly charred, then ignited over a gradually increased flame, and finally over the blast for two to five minutes. The weight

¹ Although the above is essentially the accepted procedure in commercial work, it would be better, and consume no more if as much time if the precipitation procedure given under 35. A. b (p. 258) were followed.

found represents the oxides of ferric iron, aluminum, titanium, phosphorus, and manganese, the last presumably Mn_3O_4 .

The iron, titanium, and silica in the ignited oxides are determined, after fusion with potassium or sodium pyrosulphate, exactly as detailed in 35. C (p. 259). The phosphorus and manganese having been determined in different portions (39, p. 263, and 36. B, p. 261), the aluminum oxide is found by subtracting all these oxides from the original weight of the mixture. Often the percentage reported as alumina includes in reality the titanium, phosphorus, and some of the manganese, where no attempt has been made to separately determine these.

50. CALCIUM.

The combined filtrates from the iron, aluminum, etc., are concentrated if need be to a bulk of 200 to 250 cm^3 , with occasional addition of a few drops of ammonia. If a slight precipitate separates, it is collected on a small filter, washed with water, redissolved in hydrochloric acid, and reprecipitated by ammonia. It is added to and treated with the main quantity of iron and aluminum oxides, and the filtrates are combined. To them is added while boiling 40 cm^3 (for 1 gram of sample; 20 cm^3 if but half a gram is under analysis) of a saturated solution of ammonium oxalate, and the boiling is continued until the precipitated calcium oxalate assumes a well-defined granular form. It is then allowed to stand for an hour, filtered, and washed a few times with hot water. The precipitate and filter are ignited in platinum till the oxalate is converted to oxide, which is redissolved in hydrochloric acid and the solution made up to 100 cm^3 . Ammonia is added in slight excess to the boiling solution and also ammonium oxalate to reprecipitate the lime. After an hour the oxalate is collected, washed a few times with small amounts of hot water, ignited over the blast, and weighed as the oxide.

Instead of igniting and weighing as oxide it is permissible to dissolve the oxalate in sulphuric acid, taking care to extract the filter thoroughly with hot dilute acid, and to titrate the solution with permanganate.

51. MAGNESIUM.

To the combined filtrates from the calcium precipitations are added sodium-ammonium phosphate solution in excess and, when the precipitate has formed after vigorous stirring, ammonia in considerable excess. After several hours, 12 or 15 if the precipitate is very slight, the solution is filtered, and the precipitate is redissolved in hydrochloric acid and reprecipitated by ammonia in moderate excess and a drop of the phosphate precipitant in the usual

manner. After two hours the precipitate is filtered on paper or on a Gooch filter, ignited, and weighed as pyrophosphate.

52. ALKALIES.

See 41, p. 265.

53. CARBON DIOXIDE.

See 42, p. 266.

54. SULPHUR.

See 45, p. 268.

55. WATER.

See 46, p. 269.

56. IGNITION LOSS.

The determination of ignition loss has little significance, though it affords a more or less correct indication of the proportion of carbonates in the rock. As it is a determination commonly made in commercial laboratories, some space will be devoted to it.

Loss on ignition with carbonate rocks represents, as with those of a silicate nature, the algebraic sum of a number of chemical changes involving both losses and gains, and its amount will depend largely on the temperature employed. At the temperature of a moderate blast, with crucible covered, carbon dioxide, water, and carbonaceous matter escape wholly. Sulphides are oxidized to sulphates and all the sulphur is retained as sulphate by the calcium. With a powerful blast the sulphate is decomposed gradually, with eventual loss of the entire sulphur. At this point the alkalies begin to escape as oxides, the potassium relatively faster than the sodium, and they may be found in part condensed on the lid of the crucible. If the heating is long continued they can be wholly volatilized. As a small offset to these losses the iron of pyrite and the iron and manganese of ferrous and manganous carbonates take up oxygen and unite with the lime. By proper control of the temperature it is not difficult to prevent loss of sulphur and alkalies, and this is the object to be sought in making the determination.

From 0.5 to 1 gram of the powder is placed in a platinum crucible of 20 to 25 grams weight, the crucible is inserted to three-fifths of its depth in a perforated platinum disk or asbestos board (fig. 3, p. 34), and an inclined blast flame of considerable intensity is caused to play against the bottom of the covered crucible for 15 or 20 minutes. A repetition of the heating for five minutes will usually cause little or no further loss. Duplicate determinations should agree within 0.2 per cent, and after the operator becomes skilled probably within 0.1 per cent. A muffle can be substituted for the blast. In my experiments the crucibles occupied a position 2 inches inside the closed door of the muffle. It is, however, important that each operator should ascertain just what the proper conditions may be for his particular blast or muffle. They are right if after the ignition he finds exactly the whole of the sulphur in the ignited powder in the sulphate state.

INDEX.

A.	Page.
Abrasion of crusher-----	58-59
of mortar-----	63
Absorption tubes, use of, in water determination-----	79-80
Acids, quality of-----	45
Acknowledgments to those aiding--	17
Adams, E. Q., acknowledgment to--	17, 64
(footnote)	
Adams, L. H., and Johnston, J., cited-----	55 (footnote), 231
Agulhon, H., and Bertrand G., cited--	240
Alkali bisulphates, reagents-----	46
pyrosulphates, reagents, advan- tages and disadvan- tages of-----	116 (footnote)
Alkalies, determination of-----	207-216, 265, 274
figure showing apparatus for determination of-----	209
Allen, E. T., cited-----	63, 128
Allen, E. T., and Day, A. L., cited--	70-71
pycnometer method of-----	55-57
Allen, E. T., and Johnston, J., cited--	231
(footnote)	
Allen, E. T., and Zies, E. G., cited--	239, 240
Aluminum, concealment of by man- ganese-----	134
direct determination of-----	126-130
ignition of precipitate of oxide of-----	114
precipitation of, with iron, titanium, etc-----	106-113, 257-258, 272-273
recovery of, after separation of iron as sulphide-----	126-127
from filtrates-----	113-114, 259
separation of, from iron and other elements--	127-133, 273
Aluminum chloride, volatilization of--	108
(footnote)	
Ammonia, occurrence of, in rocks---	243
Ammonia reagent, preparation of-----	45
Ammonium chloride reagent, quality of-----	46
preparation of-----	107
Ammonium oxalate reagent, quality of-----	46
Ammonium persulphate reagent, purification of--	112 (footnote)
Analysis, allowable error in-----	30
completeness and thoroughness of, importance of-----	18-24, 48-49
crushing of rock for-----	57-60
diversity of, for same rock-----	20-21
employment of air-dry powder for-----	71

	Page.
Analysis, grinding rock for-----	60-63
neglect of certain factors in, consequence of-----	22
preparation of sample for-----	57-63
quantity of sample required for--	25, 48-49, 57, 64
statement of-----	31
time required for-----	32
See also Carbonate rocks; Silicate rocks.	
Analysis, qualitative-----	41
Apparatus, glassware and porcelain, quality of-----	42
Appliances and Apparatus, descrip- tions and figures of-----	33-41
Aragonite, tests, for-----	251
Arsenopyrite, evidence as to pres- ence of, in rocks-----	230
Atterberg, A., cited-----	211 (footnote)
Auranium, substitute for platinum--	44
Austin, M., and Gooch, F. A., cited--	136
(footnote), 148, 149	
Autenrieth, W., cited-----	215

B.

Bailey, G. H., cited-----	173, 175
Balarew, D., cited-----	149
Barbier, P., method of, for separation of iron from alumi- num-----	130
Barium, determination of-----	146, 170-172, 259, 262
ignited silica, free from-----	104-105
occurrence of, in rocks-----	22, 28, 230
recovery of, from alumina pre- cipitate-----	118
from magnesium pyrophos- phate-----	152
separation of, from calcium-----	144
from calcium and mag- nesium-----	145 (footnote)
from strontium-----	145
Barium sulphate, spectroscopic test- ing of-----	172
Barnebey, O. L., method of, for fer- rous-iron determina- tion-----	206
cited-----	198 (footnote), 199, 203 (footnote)
Baskerville, C., method of, in deter- mination of titanium--	130, 131, 166
in determination of zirconium--	130, 131, 175
Baubigny, H., method of, in deter- mination of chromium--	181
Bauer, Th., cited-----	103 (footnote)

	Page.	C.	Page.
Baxter, G. P., and Kobayashi, M., cited.....	216 (footnote)	Cain, J. R., and Hostetter, J. C., cited.....	179
Bayly, R. G. W., cited.....	77	Cain, J. R., and Tucker, F. H., cited.....	179
Bechi, E., cited.....	22	Calcite, tests for.....	217, 251-252
Bellucci, I., and Grassi, L., cited.....	164	Calcium, determination of.....	140-144, 146-148, 262-263, 273
Bemmelen, J. M. van, cited.....	65 (footnote)	ignition of oxalate of.....	142
Berger, C. W., and Hulett, G. A., cited.....	102 (footnote)	precipitability of, by ammonium persulphate.....	111
Bertrand, G., cited.....	139	removal of, from magnesium pyrophosphate.....	152-153
Bertrand, G., and Agulhon, H., quali- tative test of, for boron.....	240	in alkali determination.....	236
Berzelius, J. J., method of, for fluorine.....	222-225	separation of, from magne- sium.....	140-144, 263
Beutell, A., and Blaschke, K., cited.....	65 (footnote)	separation of strontium from.....	145-146
Bisbee, H., McCaffrey, C. T., and Richards, T. W., cited.....	140, 141	Calcium chloride reagent, deteriora- tion of.....	80
Blair, A. A., crucible tongs of.....	33	Calcium fluoride, testing of precipi- tate of.....	250
Blake, G. R., and Gooch, F. A., cited.....	216 (footnote)	Calcium oxalate, solubility of.....	140-141
Blaschke, K., and Beutell, A., cited.....	65 (footnote).	Cameron, A., cited.....	98
Blast, temperature of, test of.....	103 (footnote).	Campbell, D., cited.....	151 (footnote)
Bloor, W. R., cited.....	105	Campbell, E. D., and Hess, W. H., cited.....	128
Blount, B., cited.....	102, 256	Cappel, A., cited.....	142 (footnote)
Blum, W., cited.....	107, 108, 156, 228	Carbon, determination of.....	219, 266-267
Bogitch, F., and Le Chatelier, H., cited.....	49 (footnote)	effect of, on ferrous-iron determi- nation.....	201, 203, 207, 265
Bohm, F., cited.....	210 (footnote)	occurrence of, in rocks.....	219, 250
Bolton, H. C., cited.....	251	Carbonate rocks, analysis of.....	246-274
Borck, H., cited.....	133	analysis of, defects of, as usually made.....	247-248
basic acetate method of.....	110 (footnote)	condensed forms of.....	271-274
Borgstrom, L. H., cited.....	219	detailed methods of.....	253-270
Boric oxide, fusion with.....	92-93	causes of color of.....	250
Boric oxide reagent, preparation of.....	92	ignition loss of.....	274
Bornemann, E., cited.....	80 (footnote)	importance of.....	15
Bornemann, K., and Schirmeister, H., cited.....	133	impurities in.....	249-250
Boron, determination of.....	234-241	methods of decomposing.....	253-255, 271
apparatus for determination of.....	237	mineral composition of.....	248-250
occurrence of, in rocks.....	29	qualitative composition of sili- cate rocks and.....	246-248
qualitative tests for.....	240	qualitative tests of.....	251-252
Boynton, C. N., and Gooch, F. A., cited.....	145 (footnote)	Carbonates, qualitative tests of.....	251-252
Bravo, J. J., cited.....	27 (footnote)	relative solubility of, in certain reagents.....	251
Bray, W. C., and others, cited.....	41	Carbon dioxide, determination of.....	217-219, 274
Brinton, P. H. Mc P., and Fresenius, H., cited.....	211 (footnote)	figure showing apparatus for de- termination of.....	218
Brown, James, cited.....	166	inclusions of, in rocks.....	242
Browning, P. E., cited.....	144	Carbon monoxide, evolution of, on heating rocks.....	242
Brühl, E., and Friedheim, C., cited.....	135	Carnot, A., cited.....	122
Brunck, O., cited.....	146, 148	Carron, E. C., cited.....	142 (footnote)
basic acetate method of.....	111 (footnote)	Cathrein, A., cited.....	124 (footnote)
Brush, G. J., method of, in water determination.....	77	Cavaignac, H., cited.....	90 (footnote)
Bube, K., cited.....	148	Ceramic clays, determination of iron in.....	126
Buckley, E. R., method of, for poros- ity determination.....	51, 52, 53	Cerium, detection of.....	177
Bunsen, R., cited.....	71, 98, 211 (footnote)	occurrence of, in piemontite.....	109 (footnote)
Burgess, G. K., and Sale, P. D., cited.....	44 (footnote)	in rocks.....	25, 26
Burgess, G. K., and Waltenberg, R. G., cited.....	44 (footnote)	Cerium oxalate, solubility of, in cer- tain salts.....	176 (footnote)

	Page.		Page.
Chalcopyrite, occurrence of, in rocks	28	Crucible, disk for, description and figure of	35
Chamberlin, R. T., cited	242	tongs for, description and figure of	33
Chapin, W. H., cited	234 (footnote), 235	Crucibles, platinum, loss of weight of	102 (footnote), 116 (footnote)
method of, for boron	235-240	Crushing, methods of	57-60
Chapin, W. H., and Wherry, E. T., cited	240	Crystal water. <i>See</i> Water.	
Chatard, T. M., cited	162, 179	Cumming, A. C., and Thin, R. G., cited	216 (footnote)
drying oven of, description and figure of	82	Curtis, J. S., cited	241
Chlorine, condition of, in rocks	220	Czudnowitz, C., cited	184
determination of	220-221, 267		
occurrence of, in rocks	29	D.	
Chromium, comparison of colorimetric and gravimetric methods for	183	Daniel, K., cited	222 (footnote)
determination of	170-172, 180-183, 184, 261	Daudt, H. W., cited	108 (footnote)
colorimetric	182-183	Davis, J. T., cited	175
gravimetric	181-182	Davis, W. A., cited	216 (footnote)
occurrence of, in rocks	26, 189	Davy, Humphrey, cited	92 (footnote)
precipitation of, with aluminum, etc.	106-110	Day, A. L., and Allen, E. T., cited	70-71
Citric acid, relative solubility of carbonates in	251	pycnometer method of, for specific gravity	55-57
Claasen, E., cited	185	Dehydrating agents	73-74
Clarke, F. W., cited	22	Dehydration, effect of, on physical properties	69
Classen, A., cited	46	Delesse, A., cited	242
method of, for separation of iron from titanium	133	Desiccators, use of	73
Cloedt, E. v., and Jannasch, P., cited	135	Determinations, importance of order of	48
Cobalt, detection of	136, 261	Deussen, E., cited	117 (footnote), 197 (footnote), 198
determination of	136		
occurrence of, in rocks	27	Déville, H. Ste C., cited	22
separation of, from manganese and zinc	135-136	Dieulafoy, L., cited	22, 24 (footnote), 241
Coblentz, W. W., cited	66 (footnote)	Dimitrow, P., and Karaoglanow, Z., cited	149, 151 (footnote)
Collins, W. D., and Skinner, W. W., cited	212 (footnote)	Dinwiddie, J. G., cited	226
Colorimeters, description of, and figures showing	35-41	Disk, perforated, for crucibles, description and figure of	35
Colorimetric methods, for determination of chromium	182-183	Dittrich, M., cited	30, 71, 73, 79, 94, 109, 115, 132, 139, 176 (footnote), 201 (footnote), 209
for determination of manganese	137-139	Dittrich, M., and Eitel, W., method of, for water determination	84
of titanium	155-162	Dittrich, M., and Freund, S., methods of, in separation of titanium and zirconium from iron	129, 131, 132 (footnote), 166, 175
of vanadium	157	Dittrich, M., and Leonhard, A., cited	198
comparison of colorimetric and gravimetric methods for determination of chromium	183	Döring, Th., cited	208 (footnote)
Columbium, occurrence of, in rocks	25, 30	Dolomite, definition of	247
Connor, F. M., cited	115, 209	tests for	251-252
Contamination of sample by agate by steel	63-64, 59, 60	Don, J. R., cited	242
Cooke, J. P., method of, for determination of ferrous iron	196, 204-205	Drying before analysis, uselessness of	71
method of, apparatus for, figure showing	205	Drying for hygroscopic tests, process of	73-76
Coppadoro, A., cited	119 (footnote)	Dunnington, F. P., cited	156
Copper, determination of	137, 261	Duschak, L. H., and Hulett, G. A., cited	231 (footnote)
occurrence of, in rocks	27		
separation of	135, 136	E.	
Cramer, E., and Seger, H., cited	53	Eakins, L. G., pycnometer method of for specific gravity	54
Cross, W., and others, cited	49	Eddy, E. A., and Gooch, F. A., cited	214

- | | Page. | | Page. |
|---|----------------------------------|--|---|
| Edgar, G., cited | 123 | Fresenius, H., and Brinton, P. H.
McP., cited | 211 (footnote) |
| Eitel, W., and Dittrich, M., method
of, for water determi-
nation | 84 | Fresenius, R., cited | 142 (footnote), 151 |
| Electrification of glass tubes, influ-
ence of, on weight | 80 | Freund, S., and Dittrich, M., methods
of, in separation of
titanium and zirconium
from iron | 129, 131,
132 (footnote), 166, 175 |
| Ellis, C. W. H., mortar of, descrip-
tion and figure of | 58 | Friedel, G., cited | 75 |
| Erdmann, H., cited | 242 | Friedheim, C., and Brühl, E., cited | 135 |
| Error in analysis, allowable limits
of | 30-31 | Friedheim, C., and Pinagel, A., cited | 99 |
| in calculation of feldspars | 22 | Funk, W., basic acetate method of | 111
(footnote) |
| Errors due to, abrasion of crushing
and grinding imple-
ments | 58-59, 63-64 | G. | |
| failure to determine sulphur | 23 | Galena, occurrence of, in carbonate
rocks | 249 |
| grinding of sample | 60-61,
69-71, 189-192 | Gallo, G., cited | 168 |
| variation of blast tempera-
ture | 103 (footnote) | Gases, evolution of, on heating
rocks | 242-243 |
| F. | | Gautier, A., cited | 242 |
| Faber, P., cited | 156, 161 | Gibbs, W., cited | 149 |
| Feldspars, error in calculation of | 22 | Gilbert, J. P., cited | 98, 256 |
| Ferguson, J. D., cited | 175 | Glassware, action of reagents on | 43 |
| Ferguson, J. B., cited | 125 | quality and composition of | 42 |
| Ferric chloride, volatilization of | 108
(footnote) | rules for use of | 43 |
| Ferric iron, calculation of | 123 | Glass sands, determination of iron in | 125 |
| See also Iron. | | Glucinum, occurrence of, in rocks | 25, 29 |
| Ferrous iron, determination of | 189-
207, 264-265 | Gold occurrence of, in rocks | 29 |
| determination of, hydrofluoric-
acid method of | 196-207 | substitute for platinum | 44 |
| sealed-tube method of | 193-196 | Gooch, F. A., apparatus of, for water
determination, descrip-
tion and figures of | 85-88
cited 132, 133, 234 (footnote) |
| oxidation of, by grinding | 60, 189-192 | method of, in determination of
lithium | 212-213 |
| by free oxygen in presence
of hydrofluoric acid or
a fluoride | 199-200 | in determination of ti-
tanium | 162-163 |
| preparation of sample for de-
termination of | 192 | Gooch, F. A., and Austin, M., cited | 136
(footnote), 148, 149 |
| uncertainties of determination
of | 207 | Gooch, F. A., and Blake, G. R., cited | 216
(footnote) |
| See also Iron. | | Gooch, F. A., and Eddy, E. A., cited | 214 |
| Fieldner, A. C., Selvig, W. A., and
Taylor, G. B., cited | 219,
266 (footnote) | Gooch, F. A., and Boynton, C. N.,
cited | 145 (footnote) |
| Filter paper, macerated, use of, for
precipitations | 108, 114-115 | Gooch, F. A., and Jones, L. C., cited | 234
(footnote) |
| Fischer, T., cited | 189 | Gooch, F. A., and Kobayashi, M.,
cited | 226 |
| Fluid inclusions, volatilization of | 242 | Gooch, F. A., Reckert, E. C., and
Kuzirian, S. B., cited | 105 |
| Fluorine, determination of | 222-223, 268 | Grassi, L., and Bellucci, I., cited | 164 |
| influence of, in aluminum de-
termination | 90 (footnote),
106 (footnote) | Grinder, mechanical | 61-63 |
| in silica determination | 90, 94
(footnote) | Grinding, effect of, on composition of
sample | 60-61, 69-71, 189-192 |
| occurrence of, in rocks | 29 | methods of | 60-64 |
| qualitative tests for | 222 | Gurevich, L. J., and Wichers, E.,
cited | 44 (footnote) |
| Folin, O., cited | 231 (footnote) | H. | |
| Foot, H. W., and Penfield, S. L.,
cited | 235 | Haf, R. C., and Schwartz, E. H.,
cited | 215 |
| Forchhammer, J. G., cited | 241 | Hall, R. W., cited | 102 (footnote) |
| Ford, W. E., cited | 235 | Hamberg, A., cited | 65 (footnote) |
| Foullon, H. von, cited | 241 | Harper, D. N., and Penfield, S. L.,
cited | 108 |
| Franz, B., and Streit, G., cited | 175 | | |

	Page.
Harrington, B. J., cited	252
Harrison, J. B., cited	27, 29
Hauynite, evidence as to presence of occurrence of, in rocks	230 28
Hawley, F. G., cited	99
Hayes, A. A., cited	22
Hayden, E. M., and Thornton, W. M., cited	164, 165
Heidenreich, O., and Jannasch, P., boric oxide method of, for decomposing silicates	92-93
Helium, occurrence of, in rocks	25
Hempel, W., cited	64
Hess, W. H., and Campbell, E. D., cited	128
Hewett, F., cited	27 (footnote)
Hibbert, E., cited	168
Hibbert, E., and Knecht, E., cited	123 168 (footnote)
Hildebrand, J. H., cited	126
Hinden, F., cited	252, 263
Hinrichsen, F. W., cited	94 (footnote), 167
Hintz, E., and Weber, H., cited	231 (footnote)
Holladay, J. A., cited	142 (footnote), 169
Holthof, C., cited	95, 96
Horn, D. W., cited	183 (footnote)
Horsch, M., cited	211 (footnote)
Hostetter, J. C., cited	140 (footnote), 144
Hostetter, J. C., and Cain, J. R., cited	179
Hostetter, J. C., and Roberts, H. S., electrometric method of, for iron	16, 126 (footnote)
Hüttner, K., cited	242
Hulett, G. A., and Berger, C. W., cited	102 (footnote)
Hulett, G. A., and Duschak, L. H., cited	231 (footnote)
Hundeshagen, F., method of for magnesite	263
Huybrechts, M., cited	231 (footnote)
Hydrofluoric acid reagent, quality of	45
Hydrofluoric acid method for determination of ferrous iron	196-207
Hydrogen, behavior of, on drying minerals	67
behavior of, on grinding minerals	67, 69-71
discriminating between conditions of, in minerals	64-69
evolution of, on heating rocks	242
minerals	68
rôle of, in minerals	64-69
system of classification of, in minerals	65-66
Hydrogen peroxide reagent, quality of	46
Hydrogen sulphide, as impurity in carbon dioxide	120 (footnote)
evolution of, on heating rocks	242
occurrence of, in carbonate rocks	250

I.	Page.
Hygroscopic water, determination of	73-76
See also Water.	
Iddings, J. P., cited	49
Ignition, loss by carbonate rocks on loss on, inaccuracy of water determination by	274 76-77
temperature of, variations in	103 (footnote)
Iron, correction of titanium determination for	160-131
determination of	115, 119-126, 189-207, 257-258, 264-265, 272-273.
effect of carbonaceous matter on	203, 207, 264, 265
effect of sulphides on	193-194, 201-202, 207, 233
effect of vanadium on	121-122, 202-203
electrometric method for	16, 126 (footnote)
gravimetric	124-125
volumetric	119-124, 196-207
in ceramic clays	126
in glass sands	125
Ignition of precipitate of oxide of	114
occurrence of, in carbonate rocks	248-249
precipitation of, with aluminum, etc.	106-113, 257-258, 272-273
oxidizability of divalent, by free oxygen in presence of hydrofluoric acid or a fluoride	225-226
recovery of, from filtrate	113-114
reduction of	119, 121
separation of, as sulphide	124-125
from aluminum, etc.	132-133
in titanium determination	162-163
solution of oxide of, by alkali fusion	122-123
titration of	120, 121, 123, 203-204, 260, 264-265
See also Ferric iron; Ferrous iron.	
Iron nitride, occurrence of, in lava	243
Iron oxides, error in determination of	23, 123, 189-192, 197-203, 207

J.

Jakob W., method of, in determination of chromium	181
Jannasch, P., cited	34, 80, 91, 112 (footnote)
silicate decomposition methods of	91-93
Jannasch, P., and Cloedt, E. v., cited	135
Jannasch, P., and Heidenreich, O., boric oxide fusion, method of	92-94
Jannasch, P., and Weber, H., cited	92-93, 93 (footnote)
Jannettaz, E., cited	251
Järvinen, K. K., cited	149, 151

- | | Page. | | Page. |
|--|---|--|--------------------------------|
| Manganese, determination of | 134-140, 153, 230-261, 263 | Morgan, G. T., cited | 217, 267 |
| occurrence of in rocks | 27, 248 | Morley, E. W., cited | 86 (footnote) 208 (footnote) |
| oxidizability of divalent, in presence of hydrofluoric acid | 197 | Morozewicz, J., cited | 211 (footnote) |
| precipitation of | 111-113, 135-136, 257 | Mortar, for crushing | 58 |
| removal of, from magnesium pyrophosphate | 153 | Motherwell, H. A. B., cited | 99 |
| separation of, from cobalt, copper, zinc, and nickel | 136 | Moureu, C., cited | 242 (footnote) |
| Mannich, J., and Priess, H., cited | 240 | Müller, E., and Koppe, P., cited | 139 (footnote), 197 (footnote) |
| Manning, R. J., and Lang, W. R., cited | 234 (footnote) | Murmann, E., cited | 143 |
| Mar, F. W., cited | 172 | method of, for separating calcium and magnesium | 143 |
| Marble, contamination of, by sulphides | 120 (footnote) | Murphy, R. K., and Neumanna, B., cited | 130 (footnote), 168 |
| Marrs, L. E., and Metzger, F. J., method of, for manganese | 139 | N. | |
| Marshall, H., cited | 137 (footnote) | Nepheline, detection of, in presence of olivine | 243-244 |
| Mauzelius, R., cited | 60, 70 (footnote), 189 (footnote) | Neubauer, H., cited | 148, 149, 151 |
| Meade, R. K., cited | 255 (footnote) | Neumann, B., and Murphy, R. K., cited | 130 (footnote), 168 |
| Meineke, C., cited | 98 | Neustadt, L., and Skrabal, A., cited | 145 |
| Mellor, J. W., cited | 16, 43, 126, 162, 209 | Newton, H. D., cited | 121, 122, 167 |
| Merrill, P. W., cited | 42 | Nickel, determination of | 136 |
| Merwin, H. E., acknowledgments to | 17, 64 (footnote) | occurrence of, in rocks | 27 |
| cited | 112 (footnote), 156, 157, 161, 227 (footnote) | precipitation of | 135 |
| method of, for fluorine | 227-229 | separation of, from manganese and zinc | 135-136 |
| Merwin, H. E., Johnston, J., and Williamson, E. D., cited | 251 | Nicolardot, P., and Reglade, A., cited | 173 |
| Merwin, H. E., and Posnjak, E., cited | 66 (footnote) | Nitrogen, occurrence of, in rocks | 242 |
| Merwin, H. E., Wright, F. E., and Hillebrand, W. F., cited | 68 (footnote) | Noselite, evidence as to presence of, in rocks | 230 |
| Meteorites, analysis of | 16 | occurrence of, in rocks | 28 |
| Methane, evolution of, on heating rocks | 242 | Noyes, A. A., and others, cited | 41 |
| Metzger, F. J., and Marrs, L. E., method of, for manganese | 139 | Noyes, W. A., cited | 160 |
| Microscopic examination, value of | 24 | O. | |
| Microcosmic salt reagent, quality of | 46 | Organic matter, removal of | 254 |
| Millberg, C., and Lunge, G., cited | 102, 244 | Oxidation, incompleteness of, on ignition of ferrous compounds | 76-77 |
| Mingay, J. C. H., cited | 23 (footnote) | P. | |
| Minor, J. C., and Penfield, S. L., cited | 224 | Palau, substitute for platinum | 44 |
| Mitchell, W. L., and Wells, H. L., cited | 119 (footnote) | Panichi, U., cited | 65 (footnote) |
| Mitscherlich, A., cited | 115 (footnote), 192 | Parsons, C. L., cited | 25 (footnote) |
| method of ferrous-iron determination of | 193-195 | Penfield, S. L., cited | 53, 86 (footnote) |
| Mittasch, A., basic acetate method of | 111 (footnote) | method of, for water determination | 77-79, 83 |
| Moissan, H., cited | 234 (footnote) | apparatus for, showing figures | 78, 79, 83 |
| Molybdenum, determination of | 184, 186, 261 | Penfield, S. L., and Foote, H. W., cited | 235 |
| distribution of, in rocks | 184 | Penfield, S. L., and Harper, D. N., cited | 108 |
| occurrence of, in rocks | 23, 29, 184, 250 | Penfield, S. L., and Minor, J. C., cited | 224 |
| Moore, G. E., device of, to remove air from mineral powders, description and figure of | 55-56 | Penfield, S. L., and Sperry, E. S., cited | 234 (footnote) |
| | | Perhydrol reagent, quality of | 46 |
| | | Permanganate solution, standardization of | 120 (footnote) |
| | | Peters, C. A., cited | 140 (footnote) |
| | | Peters, R., cited | 199 |

	Page.		Page.	
Pettijohn, E., and Sidener, C. F., cited	108 (footnote)	Powell, N. S., and Richards, J. W., cited	251	
Pfaff, F. W., cited	247	Pratt, J. H., method of, in ferrous- iron determination	200, 203-204	
Phenylhydrazine reagent, contami- nation of	129 (footnote)	Precht, H., cited	211 (footnote)	
Phosphoric acid, decolorant for fer- ric solutions	161	Preller, I., and Kallauner, O., cited ..	142, 143, 263	
effect of, on color of titanium peroxide	156, 159	Priess, H., and Mannich, C., cited ..	240	
Phosphorus, determination of	177-180, 263-264, 273	Pycnometer method of specific grav- ity determination	54-57	
loss of, by volatilization	116	Pyrite, effect of, on ferrous-iron de- termination	201	
occurrence of, in rocks	28, 250	insolubility of, in nonoxidizing acids	241 (footnote)	
precipitation of, with aluminum, etc	106-113, 180, 257-258	occurrence of, in rocks	28, 249	
recovery of, after separation of iron as sulphide	126-128	Pyrrhotite, evidence as to presence of, in rocks	230, 233	
separation of, from iron, tita- nium, and zirconium	126-128	occurrence of, in rocks	28	
Phosphorus salt reagent, quality of ..	46		R.	
Piedmontite, rare earths in	109 (footnote)	Radiators for evaporating solutions, description and figure of	33-35	
Pinagel, A., and Friedheim, C., cited ..	99	Radium, occurrence of, in rocks	29	
Pirsson, L. V., cited	31, 243	Ransome, F. L., cited	27 (footnote), 184 (footnote)	
and others, cited	49		Rare earths, caution against over- looking of	109 (footnote), 135
Pisani, F., cited	167, 226	determination of	170- 172, 176-177, 261	
Platino, substitute for platinum	44	occurrence of, in rocks	25, 26	
Platinum, occurrence of in rocks	25, 29	precipitation of, with aluminum, etc	106-109, 111-113	
precipitation of	105, 119 (footnote)	Rawson, F. G., method of, for separa- tion of barium and strontium from cal- cium	145	
reduction of, from solution	211 (footnote)	Reagents, quality of	45-47	
solubility of, in ferric chloride solution	105	Reckert, F. C., Gooch, F. A., and Kuzirian, S. B., cited ..	105	
Platinum crucibles, attack of, by caustic lime	147	Reglade, A., and Nicolardot, P., cited ..	173	
sodium carbonate fusion	96	Rhotanium, substitute for platinum ..	44	
loss in weight of	102 (footnote)	Richards, J. W., and Powell, N. S., cited	251	
Platinum substitutes	44	Richards, T. W., McCaffrey, C. T., and Bisbee, H., cited ..	140, 141	
Platinum ware, calcium in	44	Ridsdale, C. H., cited	122, 188	
iron in	43	Ries, H., cited	247	
quality of	43	Riggs, R. B., method of, for separa- tion of magnesium from alkalies	214	
Pope, F. J., cited	108, 109 (footnote), 162 (footnote)	Roberts, H. S., and Hostetter, J. C., electrometric methods of, for iron	16, 126 (footnote)	
Porcelain ware, action of reagents on ..	43	Robertson, J. D., cited	241	
quality of	42	Rose, H., cited	116, 223 (footnote), 242	
rules for use of	43	Rosenbladt, Th., cited	234 (footnote)	
Porosity, determination of	49, 51-53	Ross, W. H., and Wagner, C. R., cited	226	
Posnjak, E., and Merwin, H. E., cited	66 (footnote)	Rossi, J., cited	130	
Potassium, determination of	207- 211, 214-216		S.	
as chlorplatinate	210-211, 216	Sale, P. D., and Burgess, G. K., cited ..	44 (footnote)	
as perchlorate	216			
separation of, by sodium cobalti- nitrite	214-215			
Potassium bisulphate reagent, con- version of to pyrosul- phate	46			
advantages and disadvantages of	116 (footnote)			
quality of	46			
relative solubility of carbonates in	251			
Potassium pyrosulphate reagent, ad- vantages in use of	116 (footnote)			

- | | Page. | | Page. |
|---|-------------------------|--|-----------------|
| Sample, contamination of, by agate | 63-64 | Silicate rocks, decomposition of, by | |
| by steel | 58, 59 (footnote), 60 | hydrofluoric and sul- | |
| fineness of | 59, 60 | phuric acids | 89, 158 |
| preparation of | 57-63, 192 | methods of decomposition of | 89-97 |
| weight of | 64 | Siliceous limestones, character of | 249 |
| Sánchez, J. A., basic acetate method | | Silver, occurrence of in rocks | 29 |
| of | 110 (footnote) | Silvestri, O., cited | 243 |
| Sandberger, F., cited | 24 (footnote), 241 | Sive, B. E., cited | 112 (footnote) |
| Sargent, G. W., cited | 234 (footnote), 235 | Sjollema, B., cited | 255 |
| Scandium, occurrence of, in rocks | 26 | Skinner, W. W., and Collins, W. D., | |
| Schaefer, C., and Schubert, M., cited | 66 | cited | 212 (footnote) |
| (footnote) | | Skrabal, A., and Neustadt, L., cited | 145 |
| Schafgotsch's solution, character | | Smith, G. McP., cited | 231 (footnote) |
| of | 213 (footnote) | Smith, J. Lawrence, cited | 117 (footnote) |
| use of | 213-214, 233 (footnote) | method of, for alkali determina- | |
| Schaller, W. T., cited | 209 (footnote) | tion | 207-209 |
| Scherrer, J. A., and McBride, R. S., | | apparatus for, figure show- | |
| cited | 119 (footnote), 183 | ing | 209 |
| (footnote) | | Smither, F. W., and Walker, P. H., | |
| Schirmmeister, H., and Bornemann, K., | | cited | 42 (footnote) |
| cited | 133 | Smoot, A. M., cited | 231 (footnote) |
| Schreiner, O., colorimeter of, descrip- | | Sodium, determination of | 211-212 |
| tion and figure of | 39-41 | Sodium bicarbonate, fusion with | 96 |
| Schroeder, K., cited | 164 (footnote) | Sodium bisulphate, advantage and | |
| Schubert, M., and Schaefer, C., cited | 66 | disadvantage of | 117 |
| (footnote) | | (footnote) | |
| Schwartz, E. H., and Haff, R. C., | | reagent | 46 |
| cited | 215 | Sodium carbonate, effect of, on plati- | |
| Scoop. See Weighing, scoop. | | num during fusion | 96 |
| Seeman, F., cited | 223 (footnote), 225 | fusion with | 95-96 |
| Seger, H., and Cramer, E., cited | 53 | melt, effect of leaching of, with | |
| Selch, E., cited | 90 (footnote), 118 | water | 170-171 |
| Selvig, W. A., Fieldner, A. C., and | | Sodium carbonate reagent, quality | |
| Taylor, G. B., cited | 219, 266 | of | 46-47 |
| (footnote) | | Sodium cobalinitrite reagent | 215 |
| Separations, miscellaneous; alumi- | | Sodium hydroxide reagent, quality | |
| nium, iron, titanium, | | of | 47 |
| zirconium, chromium, | | Sodium phosphate reagent, quality | |
| rare earths, phospho- | | of | 46 |
| rus, vanadium | 126-134 | Sodium-potassium carbonate, com- | |
| Shimer, P. W., cited | 255 (footnote) | parison of sodium car- | |
| Shimer, P. W., and E. B., cited | 167, 169 | bonate and | 94 |
| Sidener, C. F., and Pettijohn, E., | | uses and advantages of | 117 (footnote) |
| cited | 108 (footnote) | Sodium pyrosulphate, reagent, prepa- | |
| Sievès, metal, unavailability of | 58 | ration of | 46 |
| Silica, adherence of, to dish | 100 | Solutions, heavy, unavailability of, | |
| contamination of precipitated | 104 | in specific gravity de- | |
| determination of | 89-104, 116-118, | termination of rocks | 57 |
| 226, 253-256, 259, 271 | | Sonstadt, E., cited | 211 (footnote) |
| accuracy of | 104, 118 | Spear, E. B., and others, cited | 41 |
| ignition of | 102-103 | Specific gravity, determination of | 49-57 |
| impurities in, correction for | 103 | Sperry, E. S., and Penfield, S. L., | |
| recovery of, from alumina pre- | | cited | 234 (footnote) |
| cipitate | 116-118 | Sphalerite, occurrence of in car- | |
| removal of, in fluorine determi- | | bonate rocks | 249 |
| nation | 222-223 | Starck, G., cited | 226 |
| in sulphur determination | 232 | Steiger, G., cited | 134 (footnote), |
| residue from, composition of | 104-105 | 156, 173, 199, 209 | |
| separation of, from alumina, etc. | | (footnote), 228 | |
| 97-102, 253-256, 271-272 | | colorimeter of, description and | |
| fluxes used in | 90 | figures of | 37-39 |
| solubility of | 98, 99, 101 (footnote) | drying apparatus of, description | |
| Silica, soluble, determination of | 244-245 | and figures of | 81 |
| Silicate rocks, analysis of | 18-245 | method of, for fluorine | 227 |
| analysis of, methods of | 48-245 | Steinkönig, L. A., cited | 229 |
| constituents in | 24-30 | Steinlen, R. L., cited | 208 (footnote) |

- | | Page. | | Page. |
|--|---------------------|--------------------------------------|-------------------------|
| Stierlin, R., and Lunge, G., cited | 231 | Titanium, contamination of silica by | 104 |
| | (footnote) | determination of | 154-170, 260 |
| Stoddart, C. W., cited | 232 (footnote) | colorimetric | 155-162 |
| Stokes, H. N., cited | 174, 193, | gravimetric | 162-166 |
| | 194 (footnote), 202 | volumetric | 166-170 |
| Stolberg, C., cited | 143 | loss of, by volatilization | 158 (footnote) |
| method of, for separation of cal- | | occurrence of, in rocks | 25 |
| cium and magnesium | 143 | precipitation of | 106-113, |
| Streit, G., and Franz, B., cited | 175 | | 119 (footnote), 257-258 |
| Strontium, determination of | 146, 262 | recovery of, after separation of | |
| occurrence of, in rocks | 22, 28 | iron as sulphide | 126-127 |
| separation of, from barium | 145-146 | separation of, from iron | 128-130, 133 |
| from calcium | 144-145 | from iron and aluminum | 130-132 |
| from magnesium | 140-141 | Titanium sulphate reagent, prepara- | |
| Strontium sulphate, spectroscopic | | tion of | 157 |
| testing of | 172 | Toluene bath, description and use | |
| Suleiman, A., and Wunder, H., | | of | 81, 86 |
| cited | 99 (footnote) | Tongs, crucible, description and | |
| Sullivan, E. C., and Taylor, W. C., | | figure of | 33 |
| cited | 16 | Trace, definition of | 32 |
| Sulphides, conversion of, to sulphates | | Trautmann, W., cited | 118 |
| in limestones on heat- | | Travers, M. W., cited | 242, 242 (footnote) |
| ing | 274 | Treadwell, F. P., cited | 102, 223 |
| influence of, on determination | | method of, for ferrous-iron de- | |
| of ferrous iron | 201, 207 | termination | 207 |
| Sulphur, condition of, determination | | Treadwell, F. P., and Koch, A. A., | |
| of | 230 | cited | 224, 225 |
| determination of | 170-172, | Trickett, A. B., cited | 99 |
| 230-233, 268-269, 274 | | Truog, E., and Lenher, V., cited | 99, |
| failure to determine, error aris- | | | 101, 103, 105 |
| ing from | 23 | Tschermak, G., cited | 65 (footnote) |
| fractional determination of | 233 | Tucker, F. H., and Cain, J. R., | |
| occurrence of, in rocks | 23, 28, 249 | cited | 179 |
| removal of, in alkali determina- | | Tungsten, occurrence of, in rocks | 29 |
| tion | 210 | Turner, W. A., cited | 232 |
| Sulphur dioxide reagent, quality | | Tyrolite, drying of, experiment on | 74, 75 |
| of | 186 (footnote) | | |
-
- T.
- | | | | |
|--|-----------------|------------------------------------|------------------|
| Tammann, G., cited | 65 (footnote) | U. | |
| Tantalum, occurrence of, in rocks | 25, 30 | Ullmann, C., cited | 196 (footnote) |
| Tartaric acid, relative solubility of | | Uranium, occurrence of, in rocks | 29 |
| carbonates in | 251 | | |
| Taylor, G. B., Fieldner, A. C., and | | V. | |
| Selvig, W. A., cited | 219, | Vanadium, condition of, in rocks | 184-185 |
| | 266 (footnote) | determination of, colorimetric | 189 |
| Taylor, W. C., and Sullivan, E. C., | | volumetric | 185-187, 261 |
| cited | 16 | distribution of, in rocks | 184 |
| Thin, R. G., and Cumming, A. C., | | effect of, on iron determina- | |
| cited | 216 (footnote) | tion | 121-123, 202-203 |
| Thörner, T. W., cited | 53 | failure to determine, error from | 22-23 |
| Thorium, occurrence of, in rocks | 25, 29 | occurrence of, in rocks | 22, 26, 184, 250 |
| separation of, from iron | 129 | precipitation of, with aluminum, | |
| Thornton, W. M., cited | 127 (footnote), | etc. | 106-113 |
| 164, 165, 175 | | qualitative tests for | 187 |
| method of, for titanium | 164-166 | Veitch, F. P., cited | 90 (footnote) |
| Thornton, W. M., and Hayden, E. M., | | Vogt, J. H. L., cited | 193 |
| cited | 164, 165 | Volhard, J., cited | 134 (footnote) |
| Thorpe, T. E., cited | 22 | | |
| Thugutt, St. J., cited | 65 (footnote) | W. | |
| Tin, occurrence of, in rocks | 25, 29 | Wagner, L. R., and Ross, W. H., | |
| Titanic oxide, solubility of, in alka- | | cited | 226 |
| lies | 132 | Wagoner, L., cited | 242 |
| | | Walker, P. H., and Smither, F. W., | |
| | | cited | 42 (footnote) |
| | | Waltenberg, R. G., and Burgess, | |
| | | G. K., cited | 44 (footnote) |
| | | Walters, H. E., cited | 137 (footnote) |

	Page.		Page.
Walton, J. H., Jr., cited.....	161	Wheeler, H. A., and Luedeking, C., cited	243
Warth, H., cited.....	77 (footnote)	Wherry, E. T., acknowledgments to	17, 64 (footnote)
Washington, H. S., cited.....	16, 19 (footnote), 20 footnote), 24 (footnote), 25, 29, 30, 31, 120 (footnote), 134 (footnote).	cited	234 (footnote)
method of, in crushing.....	59	Wherry, E. T., and Chapin, W. H., cited	240
in determination of phos- phorus.....	178	Wherry, E. T., and Larsen, E. S., cited	69 (footnote)
Washington, H. S., and others, cited.....	49	Wichers, E., cited.....	96
Water, direct determination of....	79-80, 267, 269-270, 274	Wichers, E., and Gurevich, L. J., cited	44 (footnote)
direct determination of, appa- ratus for, description and figures of.....	81-90	Wilke-Dörfurt, E., cited	208 (footnote)
discriminating between condi- tions of, in minerals....	64-69	Williamson, J. A., cited.....	45 (footnote)
distilled, quality of.....	47	Williamson, E. D., Johnston, J., and Merwin, H. E., cited....	251
inclusion of hygroscopic, in sum- mation.....	72	Winkler, L. W., cited.....	231 (footnote)
indirect determination of.....	73-77	Wright, F., Hillebrand, W. F., and Merwin, H. E., cited	68 (footnote)
methods of determination of....	73-89	Wülfing, E. A., cited....	193, 213 (footnote)
rôle of, in minerals.....	64-69	Wunder, M., and Suleiman, A., cited	99 (footnote)
suspension in, determination of specific gravity by....	50-53	Y. Yttrium, occurrence of, in rocks....	26
system of classification of, in minerals	65-66	Z. Zambonini, F., cited.....	65 (footnote)
behavior of, on drying minerals..	67-68	Zeolitic minerals, dehydration of....	75-76
on heating minerals.....	68	occurrence of, in rocks....	51 (footnote)
lost by grinding.....	59 (footnote) 67, 69-71	Zies, E. G., and Allen, E. T., cited..	239, 240
taken up by grinding..	60-61, 67, 69-71	Zimmerman, C., method of, for sep- aration of magnesia....	213
Waters, C. E., cited.....	42	Zinc, determination of.....	136, 261
Weber, H., and Hintz, E., cited....	231 (footnote)	occurrence of, in rocks.....	29, 249
Weber, H., and Jannasch, P., boric oxide, method of, for decomposing silicates	92-93, 93 (footnote)	precipitation of.....	135
Weighing, scoop for, description and figure of	35	separation of, from manganese	136
Weiss, L., and Kaiser, H., cited....	127, 156	Zinc oxide solution, preparation and use of	213-214, 233
Weller, A., method of, for determi- nation of titanium.....	155	Zirconium, determination of.....	172-176
Wells, H. A., and Mitchell, W. L., cited.....	119 (footnote)	difficulty with, in gravimetric determination of ti- tanium	163
Wells, R. C., cited.....	157 (footnote)	occurrence of, in rocks.....	26, 172
Wells, J. S. C., and Lenher, V., cited	240	precipitation of, with aluminum, etc.	106-113
		recovery of, after separation of iron as sulphide.....	126-123
		separation of, from iron..	128-130, 133
		from iron and aluminum..	130-132

Y.

Yttrium, occurrence of, in rocks.... 26

Z.

Zambonini, F., cited..... 65 (footnote)
 Zeolitic minerals, dehydration of... 75-76
 occurrence of, in rocks... 51 (footnote)
 Zies, E. G., and Allen, E. T., cited... 239, 240
 Zimmerman, C., method of, for sep-
 aration of magnesia... 213
 Zinc, determination of..... 136, 261
 occurrence of, in rocks..... 29, 249
 precipitation of..... 135
 separation of, from manganese 136
 Zinc oxide solution, preparation and
 use of

213-214, 233
 Zirconium, determination of..... 172-176
 difficulty with, in gravimetric
 determination of ti-
 tanium

163
 occurrence of, in rocks..... 26, 172
 precipitation of, with aluminum,
 etc. 106-113
 recovery of, after separation of
 iron as sulphide.... 126-128
 separation of, from iron 128-130, 133
 from iron and aluminum 130-132



